



SCHOOL of
GRADUATE STUDIES
EAST TENNESSEE STATE UNIVERSITY

East Tennessee State University
Digital Commons @ East
Tennessee State University

Electronic Theses and Dissertations

Student Works

8-2010

Cyanoscorpionates and Transition Metal Complexes.

Donald Martin Johnson
East Tennessee State University

Follow this and additional works at: <https://dc.etsu.edu/etd>



Part of the [Inorganic Chemistry Commons](#)

Recommended Citation

Johnson, Donald Martin, "Cyanoscorpionates and Transition Metal Complexes." (2010). *Electronic Theses and Dissertations*. Paper 1725. <https://dc.etsu.edu/etd/1725>

This Thesis - Open Access is brought to you for free and open access by the Student Works at Digital Commons @ East Tennessee State University. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of Digital Commons @ East Tennessee State University. For more information, please contact digilib@etsu.edu.

Cyanoscorpionates and Transition Metal Complexes

A thesis
presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Master of Science in Chemistry

by
Donald Martin Johnson Jr.

August 2010

Dr. Ningfeng Zhao, Chair

Dr. Jeffrey Wardeska

Dr. Yu-Lin Jiang

Keywords: Cyanoscorpionate, Polypyrazolyborate

ABSTRACT

Cyanoscorpionates and Transition Metal Complexes

by

Donald Martin Johnson Jr.

The new dihydrobis(4-cyano-3-tert-butylpyrazolylborate) ligand has been synthesized. Isolated crystals of the thallium complex were collected and structurally characterized by X-ray diffraction. Transition metal complexes of the ligand are currently under investigation.

CONTENTS

	Page
ABSTRACT	2
LIST OF FIGURES	5
Chapter	
1. INTRODUCTION	6
Overall Introduction	6
Material Science	7
Polypyrazolylborates	9
Cyanoscorpionate Polymers	12
2. THE LIGAND	14
Pyrazole Synthesis	15
Cyanoscorpionate Synthesis	22
Thallium Complexes	29
3. TRANSITION METAL COMPLEXES	42
The $(\text{Bp}^{\text{t-Bu}, 4\text{CN}})_2\text{Cu}$ Complex	43
Method A	43
Method B	48
Future Research	53
Experimental	53
General Experimental	53
Synthesis of $\text{Hpz}^{\text{t-Bu}, 4\text{CN}}$	54
Synthesis of $\text{Hpz}^{\text{Ph}, 4\text{CN}}$	56
Synthesis of $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{K}$	56
Synthesis of $\text{Bp}^{\text{Ph}, 4\text{CN}}\text{K}$	57
Synthesis of $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{Tl}$	58

Chapter	Page
Growth of $\text{Bp}^{\text{Ph}, 4\text{CN}}\text{Tl}$ Crystals	58
Transition Metal Complexes	59
Method A	59
Method B	60
4. CONCLUSIONS	61
BIBLIOGRAPHY	63
VITA	65

LIST OF FIGURES

Figure	Page
1. Polypyrazolyborate	10
2. Cyanopyrazole Synthesis	15
3. IR of $\text{Hpz}^{t\text{-Bu}, 4\text{CN}}$	17
4. NMR of $\text{Hpz}^{t\text{-Bu}, 4\text{CN}}$	18
5. IR of $\text{Hpz}^{\text{Ph}, 4\text{CN}}$	20
6. NMR of $\text{Hpz}^{\text{Ph}, 4\text{CN}}$	21
7. Synthesis of $\text{Bp}^{\text{R}, 4\text{CN}}\text{K}$	22
8. IR of $\text{KBp}^{t\text{-Bu}, 4\text{CN}}$	24
9. NMR of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{K}$	25
10. IR of $\text{Bp}^{\text{Phen}, 4\text{CN}}\text{K}$	27
11. NMR of $\text{Bp}^{\text{Phen}, 4\text{CN}}\text{K}$	28
12. Synthesis of $\text{Bp}^{\text{R}, 4\text{CN}}\text{Tl}$	29
13. IR of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$	31
14. NMR of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$	32
15. ORTEP Mercury drawing of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$	35
16. ORTEP Mercury drawing of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$ bottom view	36
17. ORTEP Mercury drawing of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$ of close contact	37
18. IR of $\text{Bp}^{\text{Ph}, 4\text{CN}}\text{Tl}$	38
19. NMR of $\text{Bp}^{\text{Ph}, 4\text{CN}}\text{Tl}$	39
20. Synthesis of $(\text{Bp}^{t\text{-Bu}, 4\text{CN}})_2\text{Cu}$	43
21. IR of $(\text{Bp}^{t\text{-Bu}, 4\text{CN}})_2\text{Cu}$ Method A	45
22. IR of $(\text{Bp}^{t\text{-Bu}, 4\text{CN}})_2\text{Cu}$ Flat Crystals from Method A	47
23. IR of Red/Brown Precipitate from Method B	49
24. IR of Soluble Green Precipitate from Method B	51

CHAPTER 1

INTRODUCTION

Overall Introduction

Over the past 44 years there has been much progress in the development of polypyrazolylborates.¹ This group of ligands, more commonly known as scorpionates, is perhaps one of the most valued ligands used in material science to date. The nature of these ligands provides chemists with much room for creativity and precise tuning of desired properties. Uses for scorpionates span a broad range of fields such as the production of electronic and magnetic materials, bioinorganic, catalytic, organometallic, and inorganic chemistry. In addition to their versatility, it is well appreciated that scorpionate ligands are generally easily attained through the use of low temperature synthetic procedures.

Our research focuses on scorpionates substituted with cyano functional groups. The cyano substituent possesses two very useful qualities we wish to explore. The first property of interest is the strong electron-withdrawing ability. Scorpionates readily chelate transition metals to form stable complexes. An electron withdrawing substituent on the pyrazole ring will pull electron density from the chelating nitrogen atoms, affecting the electronic and magnetic properties of the entire coordination sphere. In addition to electronic activity, the cyano group will provide the opportunity to create multinuclear transition metal complexes and coordination polymers by the chelation of a second metal ion. The bond network creates a fully conjugated path between metal ions that should provide a means of communication between the metal centers, and produce molecular materials that carry both bulk magnetic and

electrical properties.¹

Material Science

As our society progresses in technology the need for new types of material increases. Among all of the properties that can be associated with a material, magnetism and electrical conductivity are perhaps two of the most important ones. While atomic materials are the most prevalent and most widely encountered magnetic and electrically conductive materials, they have many disadvantages over molecular materials. Atomic materials are usually made using high temperature metallurgic processes, are heavy, and cannot be made flexible nor transparent. Molecular materials can be made through low temperature synthetic procedures, have light weight, and have the potential to be designed with flexibility or transparency. The production of good quality molecular magnets and conductive polymers would be both lucrative and the next breakthrough in material science.² For cyanoscorpionates, the potential for bulk magnetism and electrical conductivity stem from the fully conjugated pathway between two metal moieties.³ To gain a better grasp of the mechanism it is necessary to discuss the concepts behind molecular magnets and conductive polymers.

The magnetic properties of a material are based on its ability to couple the spins of unpaired electrons on neighboring atoms. Electrons have a spin of plus or minus $\frac{1}{2}$. If all spins are ferromagnetically aligned, then the unpaired electrons of the two atoms are all spin up or all spin down. The vectors then add to create a net spin. Antiferromagnetic interactions occur when the electrons align with opposite spins, resulting in a net spin of zero. Similar to ferromagnetism, there also exists a third type of magnetic interaction

called ferrimagnetism. The magnetic interaction presents itself in molecular based magnets when two units of unequal spin magnitudes couple antiferromagnetically. The result of such an interaction is a net spin other than zero. Traditionally, these properties have been exploited by manipulating atom based materials. Atom base units are thought of as being small individual magnets. These units align their spin through space, coupling with one another to produce a bulk magnet. Recently however, molecular magnets have become an area of great interest.

To exhibit bulk magnetism, it is essential that the net spins are aligned in three dimensions. Due to the antiferromagnetic interaction between electrons in sigma and pi bonds, molecular based magnets have remained somewhat elusive. Some free radical ions in conjunction with charge transfer salts have been creatively arranged to allow through space ferromagnetic coupling between cations and anions. The arrangement in these molecules like $[M^+CP^*_2]^{+\cdot}[TCNQ]^{-\cdot}$ (where M^+ is the metal ion, CP is a cyclopentadienyl-like ligand, and TCNQ is 7,7,8,8-tetracyanoquinodimethane) allows for the spins to align in three dimensions by ferromagnetically coupling the one dimensional polymer chains together.² The type of arrangement we are looking to create is quite different in that the metal to metal interactions will occur via the fully conjugated bond network, not through space.³

Coordination polymers with both a fully conjugated pathway between transition metal ions, and coupling between metals of different spin states can induce ferrimagnetic behavior. The fully conjugated pathway provides a means of "communication" between the metal centers, giving the opportunity for electronic coupling. If the spin on one metal is $S = 5/2$ and the spin on the second metal is $s = 1/2$, as it is with the zigzag chain of alternating Mn^{+2} and $Cu(opba)^{-2}$ ions in $MnCu(opba)(DMSO)_3$, where opba is

o-phenylenebis(oxamato), antiferromagnetic interactions will yield a net spin of $S = 2$.⁴ This metal to metal interaction through the fully conjugated pathway is the mechanism by which cyanoscorpionate coordination polymers will obtain bulk magnetism.³

When using atoms as the base unit for conductors, the atoms are arranged in a crystal lattice structure. The lattice structure allows the valence electrons to occupy the antibonding orbitals. The lattice can then be thought of as a network of cations with a cloud or sea of electrons freely moving from one atom to the next. If an electrical potential is placed at opposite ends of the network, electronic movement will occur. A continual source of electrons is supplied at the anode while electrons in the cloud are drawn toward the cathode. Polymeric conductivity is less understood but is known to depend upon fully conjugated networks of spatially extended pi bonds. The conjugated pathway of macromolecules like polyacetylene provides a chain of partly filled orbitals that can transfer electrons.⁵ It is theorized that a similar conjugated pathway can be made by forming cyanoscorpionate transition metal coordination polymers.³

Polypyrazolyborates

In the mid-1960s Trofimenko discovered a new ligand with two to four pyrazole rings bound to a central boron atom as illustrated in Figure 1.⁶ These monoanionic ligands were found to readily chelate transition metal ions. The pyrazole molecule is a five membered aromatic ring, made up of two nitrogen and three carbon atoms. Substituents can be placed on the number three, four, and five positions of the pyrazole ring. Due to the nature of the pyrazole ring structure, a wide combination of substituents can be used for the manipulation of electronic and magnetic properties of

the ligand metal complexes.¹

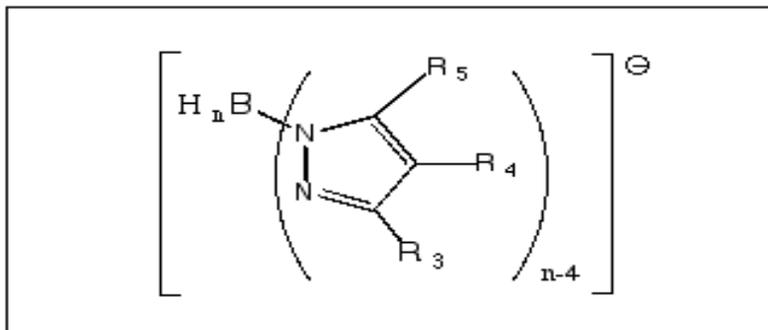


Figure 1 Polypyrazolylborate

Each pyrazole attached to the boron can be identical or different. A scorpionate ligand with all identical pyrazole rings is called a homoscorpionate and one consisting of different pyrazole rings is considered a heteroscorpionate. Because each pyrazole ring can have up to three different substituents, the ligand is therefore left with many possible combinations and a remarkable amount of versatility.

The specific nomenclature and abbreviations used for polypyrazolylborates should be discussed, as they will be used from here on. The disubstituted ligand, dihydrobispyrazolylborate, is written as Bp. The trisubstituted and tetrasubstituted varieties are abbreviated as Tp and pzTp, respectively. If all substituents are different, they are written as superscripts with the position number written before each substituent. With the exception of a pyrazole containing three different substituents, it is not necessary to put the number 3 before the substituent of the 3 position. All other positions must be preceded with the number corresponding to its position. Dihydrobis(3-*tert*-butyl-4-cyano-5-methylpyrazolyl)borate would be abbreviated as Bp^{3*t*-Bu, 4CN, 5Me}, while dihydrobis(3-*tert*-butyl-4-cyanopyrazolyl) borate would be written as Bp^{*t*-Bu, 4CN}. If the same type of substituent is occupying the 3 and 5 positions,

the substituent name is written as a superscript followed by the number 2. For example dihydrobis(3,5-*tert*-butylpyrazolyl)borate would be written as $\text{Bp}^{\text{t-Bu}2}$.⁷

Bulky alkyl and aryl groups such as *tert*-butyl, *iso*-propyl, and phenyl groups have been used to attach to the number 3 carbon atom. Though they are not electronically active, it has been demonstrated that once the scorpionate metal complex is formed the steric effects from these bulky groups greatly affect the electronic and magnetic properties of the complex.¹ The steric bulk will push the metal ion away, lengthening the nitrogen-metal bonds. The longer bond distances have been associated with spin crossover properties. This phenomena was observed with Tp_2Fe complex as increasingly bulky groups were substituted on the number 3 position.⁶ Research has been done exploring the effects of substituting these alkyl and aryl groups on the ligand, but it was not until the mid 1990s, when Diaz and others began working with the CF_3 group that electron withdrawing substituents became an area of investigation. The study of the CF_3 groups substituted on the 3 and 5 positions revealed some remarkable properties including lengthening of the nitrogen-metal bond and reduced backbonding between the metal and a coordinated carbon monoxide.⁸

To further expand the potential uses of the ligand, Trofimenko and others decided to substitute a cyano group on the number 4 carbon.⁹ As with CF_3 , the cyano group is by no means electronically innocent. The electron withdrawing properties of the cyano group greatly influenced the electron donating capabilities of the ligand, thus affecting the ligand metal bonds. In addition to its electronic activity, the nitrogen atom of the cyanide is known for its ability to form coordination bonds to transition metals, a property not exhibited by the CF_3 group. The ability to ligate to a second metal ion gives rise to the formation of a

coordination polymer. It is hoped that the electron withdrawing capabilities of the cyano group will influence the metal complex as the CF_3 did by pulling electron density from the ring, thus elongating the nitrogen-metal bonds. Substituents can also be placed on the number 5 carbon. While steric effects will not play much of a role for the 5 position, electron withdrawing substituents will, as demonstrated by the CF_3 group.³ Currently however, no synthetic procedures have been explored that include a cyanide on the number 5 carbon, so the position will be left unsubstituted.

Cyanoscorpionate Polymers

Trofimenko and others worked on creating the $\text{Bp}^{4\text{CN}}$ ligand due to its electron withdrawing properties in conjunction with its affinity for coordination with transition metals. Upon formation of the transition metal complexes the product polymerized resulting in an intractable precipitate.⁹ The polymerization was proof of concept that the cyano group could coordinate to a second metal center. The introduction of the bulky group on the 3 position not only lengthens the bond between the pyrazole nitrogen and the metal but also provides the steric hindrance that prevents the uncontrolled polymerization of the cyanide group.¹ It is therefore necessary to find a way to polymerize the cyanopyrazoles with bulky substituents.

In addition to forming the transition metal complexes, the $(\text{Bp}^{\text{Ph}, 4\text{CN}})_2\text{Cu}$ complex has also been polymerized using $\text{Rh}_2(\text{CF}_3\text{COO})_4$. The $\text{Rh}_2(\text{CF}_3\text{COO})_4$ is well known for its ability to coordinate with cyano groups.¹⁰ While this coordination polymer does not meet all the criteria to make a conductive polymer, it does provide a proof of concept that cyanoscorpionates with bulky substituents can be used to form coordination polymers. A recent

discovery by Bullinger and Eichhorn even furthers this notion that cyanoscorpionates can form conductive coordination polymers. The article describes their achievement in creating the first cyanoscorpionate ligand-metal complex coordinated only through the nitrogen of the cyanide group. The 2:1 ligand-to-metal complex of $\text{Tp}^{t\text{-Bu}, 4\text{CN}}$ was coordinated in a trans orientation about the meta center. Complexes of this configuration were made with Co^{2+} , Mn^{2+} , and Ni^{2+} . This new motif could give us insight on the formation of homometallic and heterometallic coordination polymers of the cyano-substituted scorpionate ligands. Synthesis of new cyanoscorpionate heterometallic coordination complexes expand the research area, making the ligand even more versatile. Heterometallic coordination polymers with a fully conjugated pathway may allow for the synthesis of ferrimagnetic materials.¹¹ As earlier discussed, the fully conjugate network between metal centers provides an avenue for the movement of electrons. This spatially extended pi bonding network also allows for coupling between metal ions resulting in ferrimagnetic coupling. To attain the maximum amount of bulk magnetism it may be necessary to make two dimensional sheet polymer for the alignment of the electron spins in three dimensions.² Cyanoscorpionates are quite unique in that they allow for both possibilities of a making a molecular magnet and a conductive polymer.³ Our goal is to further explore the effects of cyano substitution on scorpionate ligands by producing and structurally characterizing a new cyanoscorpionate ligand, dihydrobis(3-*tert*-butyl-4-cyanopyrazolyl)borate, and its transition metal complexes.

CHAPTER 2

THE LIGAND

The $\text{Tp}^{\text{Ph}, 4\text{CN}}$, $\text{Tp}^{t\text{-bu}, 4\text{CN}}$, and $\text{Bp}^{\text{Ph}, 4\text{CN}}$ ligands have previously been reported by Eichhorn and others.^{1,3} We decided to make the $\text{Bp}^{t\text{-bu}, 4\text{CN}}$ in order to finish the "set" for comparison and gain more insight as to how the electronically active cyano substituents in conjunction with the bulky groups influence the electronic properties of the transition metal complexes. Though the $\text{Bp}^{\text{Ph}, 4\text{CN}}\text{Tl}$ complex has previously been synthesized, it has never been structurally characterized.³ Providing the crystallographic data for the structure would be of great benefit as it could be used for further comparison. Our attempts to attain x-ray quality crystals of the complex are promising but inconclusive as of yet. The *tert*-butyl group is the more sterically bulky, so it will tend to push the metal further away from the nitrogen than the phenyl group can. Ideally, the addition of another bulky group, a third pyrazole, to the ligand should make the bond lengthen as well. Trisubstituted scorpionates have the stabilizing property of forming a "pocket" upon chelation. This pocket effect is not present in the disubstituted form and may be a contributing factor in the ligand metal bond distances. The potassium complexes of scorpionates are quite difficult to crystallize due to the size of the cation. In contrast, the thallium cation is much larger and should therefore be more easily crystallized. Once the ligand is made, we hope to use it further to create transition metal complexes. We also hope to see evidence in the $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$ crystal structure implying that the cyano group on the pyrazole will allow us to later form multinuclear transition metal complexes and coordination polymers exhibiting both bulk magnetic

properties and electrical conductivity.

Pyrazole Synthesis

Cyano substituted pyrazoles can be synthesized using several different techniques. The main problem with most techniques is that they use very toxic phosgene or explosive diazomethane.⁷ To avoid the use of such dangerous chemicals, we used the modified version of the Tupper and Bray synthesis as described by Zhao, Stipdonk, and Eichhorn in their paper on $\text{Hpz}^{\text{t-Bu}, 4\text{CN}}$ synthesis. As shown in Figure 2, changing the R group in the first step is the only modification needed to make pyrazoles with differing bulky groups substituted in the 3 position.¹² The synthesis worked quite well to produce the *tert*-butyl and phenyl substituted versions. From past and present experience, the synthesis seems to only work so long as the bulky R group does not contain any alpha hydrogen atoms. As in previous

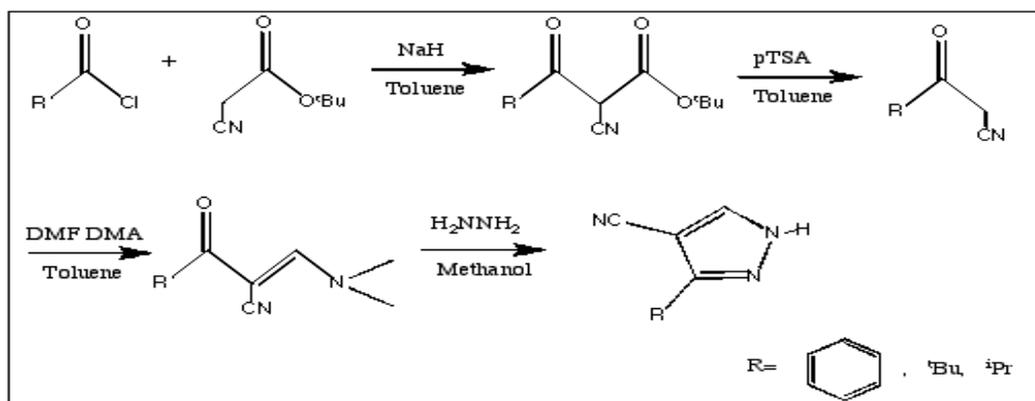


Figure 2 Cyanopyrazole Synthesis

attempts using the methyl group by Zhao¹³, our attempts using the isopropyl substituent were unsuccessful. It is evident that in the final step, the alpha hydrogen of the isopropyl group, is acidic and is preventing the formation of the pyrazole.

By starting with trimethylacetyl chloride, we were able to create a

product that had the characteristic IR cyano stretch at 2226.93 cm^{-1} as shown in Figure 3. The ^1H NMR spectra, in Figure 4, shows the *tert*-butyl peak at 1.5 ppm with an integration of 1 and the hydrogen on the number 5 position of the pyrazole at 7.85 ppm with an integration of 0.1 in.

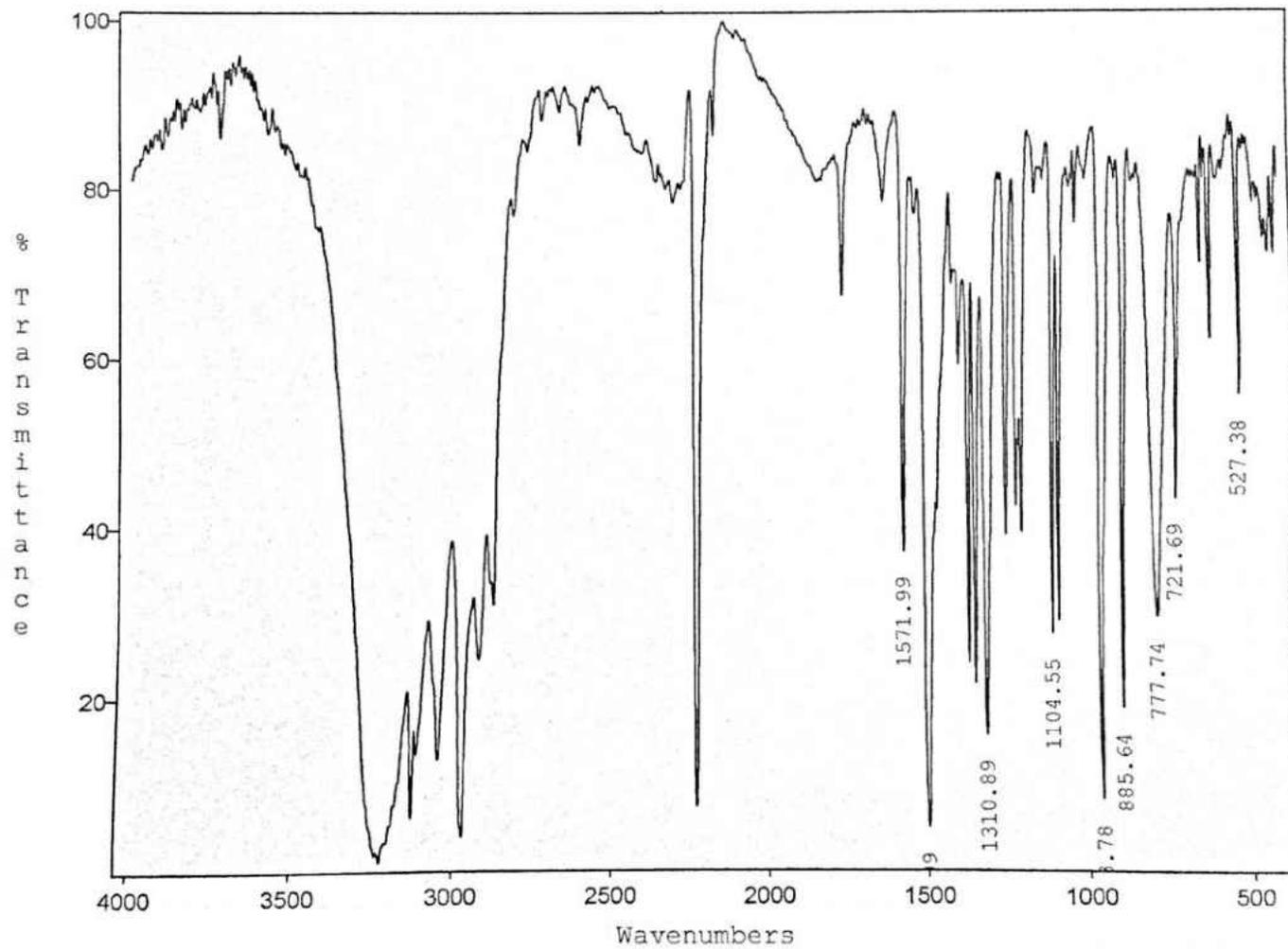
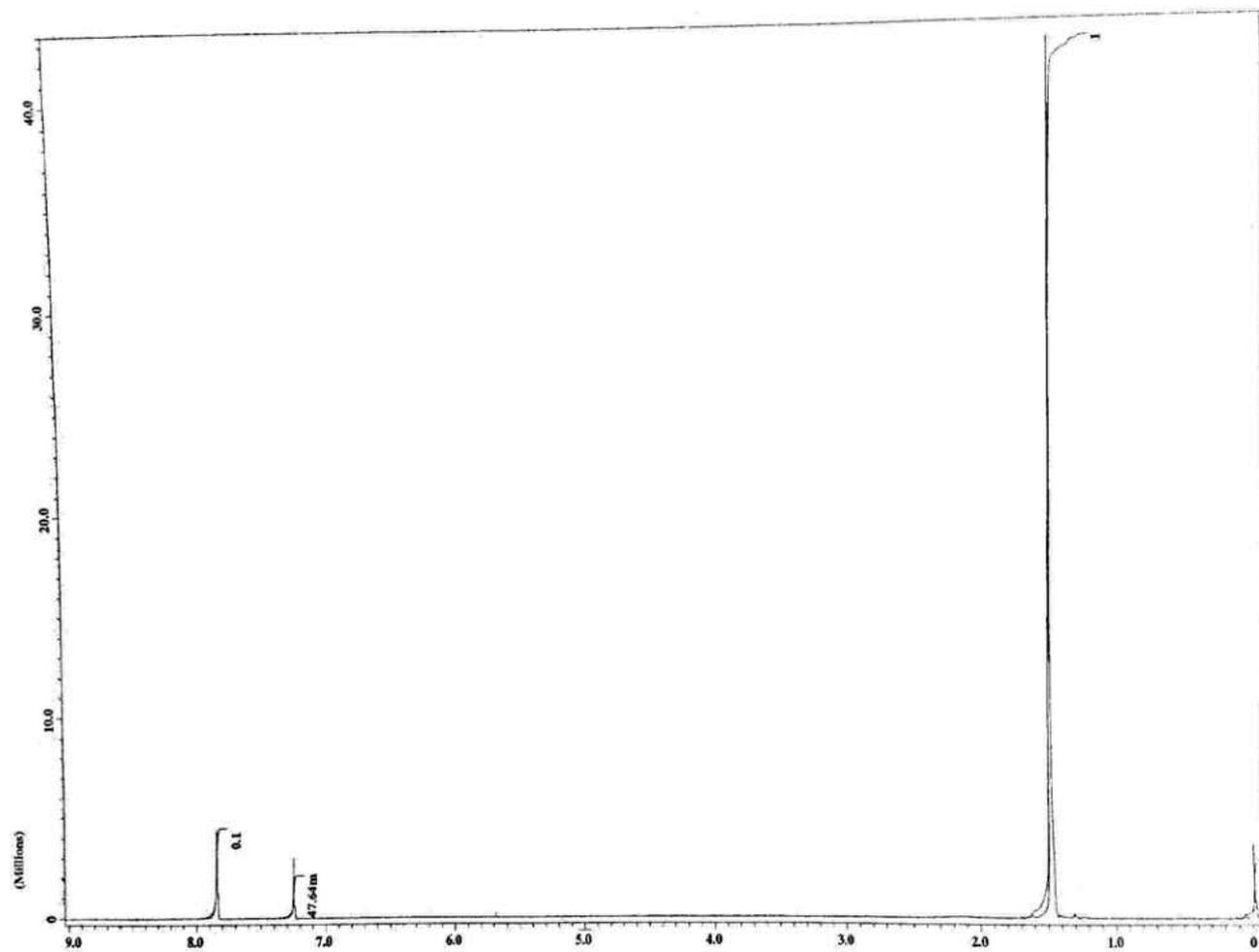


Figure 3 IR of Hpz^{t-Bu,4CN}



X : parts per Million : 1H

Figure 4 ^1H NMR of $\text{Hpz}^{\text{t-Bu}, 4\text{CN}}$

To make the phenyl substituted cyanopyrazole we exchanged the trimethylacetyl chloride for benzoyl chloride. Following the synthesis through, we ended with a product that had the characteristic IR and ^1H NMR peaks. The IR spectra from Figure 5 shows the cyano stretch at 2226.93 cm^{-1} while the ^1H NMR multiplets at 7.50, and 7.55 ppm with the doublet at 7.89 ppm in Figure 6 correspond to the phenyl ring. The singlet at 8.55 ppm on the NMR is characteristic of the hydrogen on the number 5 position of the pyrazole ring. DMSO- d_6 shows up as a singlet at 2.5 ppm. Due to the hygroscopic nature of the solvent, there is also a water peak at about 3.4 ppm.

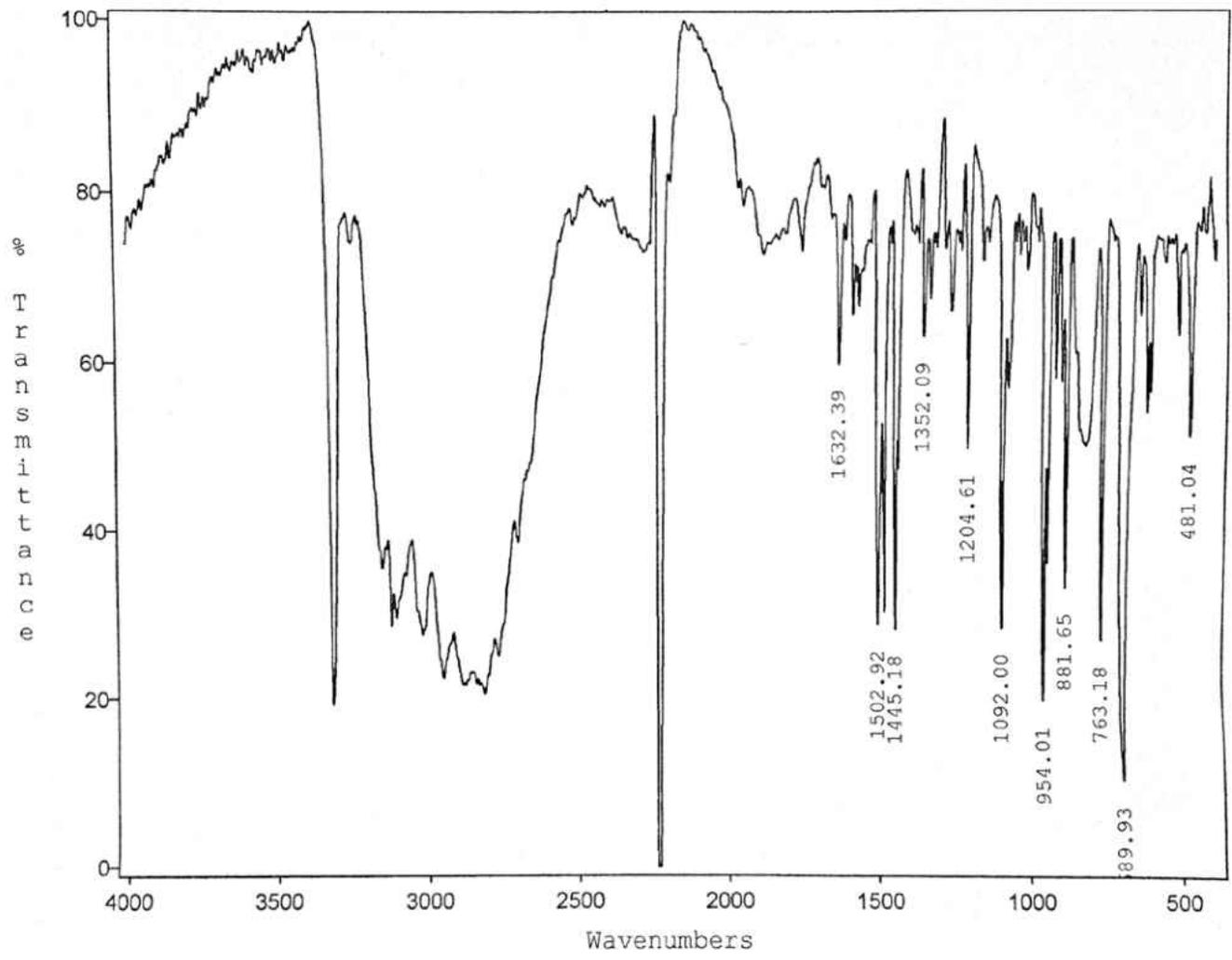


Figure 5 IR of Hpz^{Ph, 4CN}

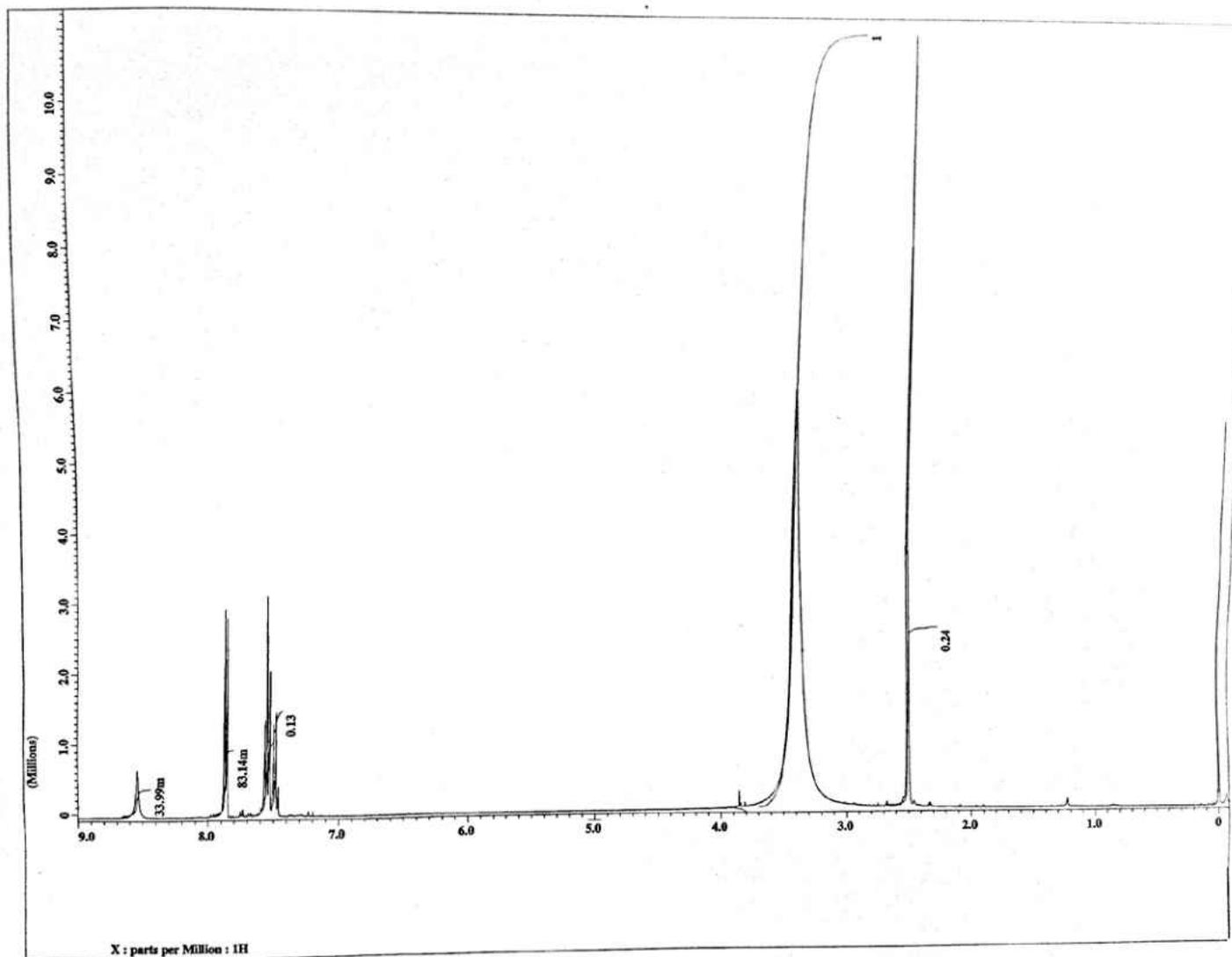


Figure 6 ^1H NMR of $\text{HpZ}^{\text{Ph}, 4\text{CN}}$

Cyanoscorpionate Synthesis

The potassium complexes of $Bp^{t-Bu,4CN}$ and $Bp^{Ph,4CN}$ were synthesized as illustrated in Figure 7. The pyrazole was melted with potassium borohydride in a 2:1 ratio, respectively. The only differences in procedure are the reaction temperatures and the pyrazole used as the starting material.

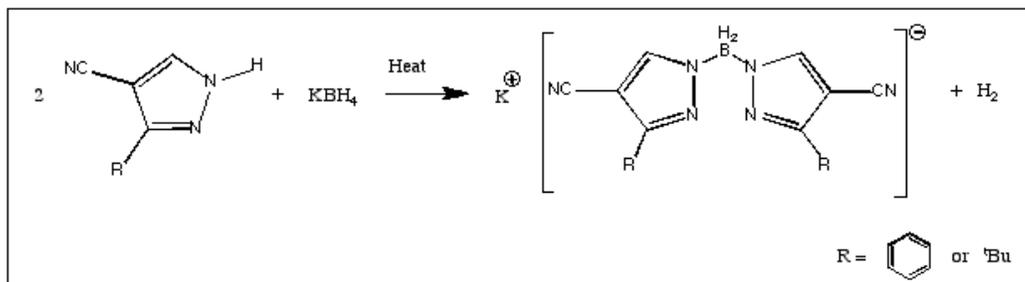


Figure 7 Synthesis of $Bp^{t-butyl,4CN}K$

To form the potassium dihydrobis(3-tert-butyl-4-cyanopyrazolyl)borate the mixture was heated to 130°C and stirred for one hour. At about 120°C the pyrazole melted. Hydrogen gas bubbles were observed as the reaction proceeded. Special care was taken not to exceed 130°C as higher temperatures could lead to the formation of the $Tp^{t-Bu,4CN}$ ligand.

The product resolidified after about 30 minutes of stirring. Acetonitrile was then used to dissolve the product and the solution was filtered to remove any unreacted potassium borohydride. Once the solvent was removed under reduced pressure, a small amount of THF was added to fully dissolve the product. Toluene was then added to the solution to precipitate the $Bp^{t-butyl,4CN}K$ product, leaving the excess pyrazole in solution. The product was filtered out of solution, suspended in boiling Toluene, and then filtered again to further purify the ligand. The end product was a very fine white powder. The IR and 1H NMR spectra in Figure 8 and Figure 9, respectively, indicate that the product is $Bp^{t-Bu,4CN}K$. The

IR spectra show B-H stretches at approximately 2436 and 2403 cm^{-1} along with the cyano stretch at about 2225 cm^{-1} . The ^1H NMR spectra show characteristic peaks for the *tert*-butyl group at about 1.3 ppm with an integration of 1 and the number 5 hydrogen at 7.9 ppm with an integration of .11. The ^1H NMR spectra also contains a toluene singlet at 2.3 ppm with accompanying multiplets at about 7.18 and 7.25 ppm, a DMSO- d_6 peak at approximately 2.5 ppm, and a water peak at about 3.37 ppm. The water peak is thought to be present due to the hygroscopic nature of the DMSO- d_6 . The presence of toluene was due to the final purification step prior to sample preparation.

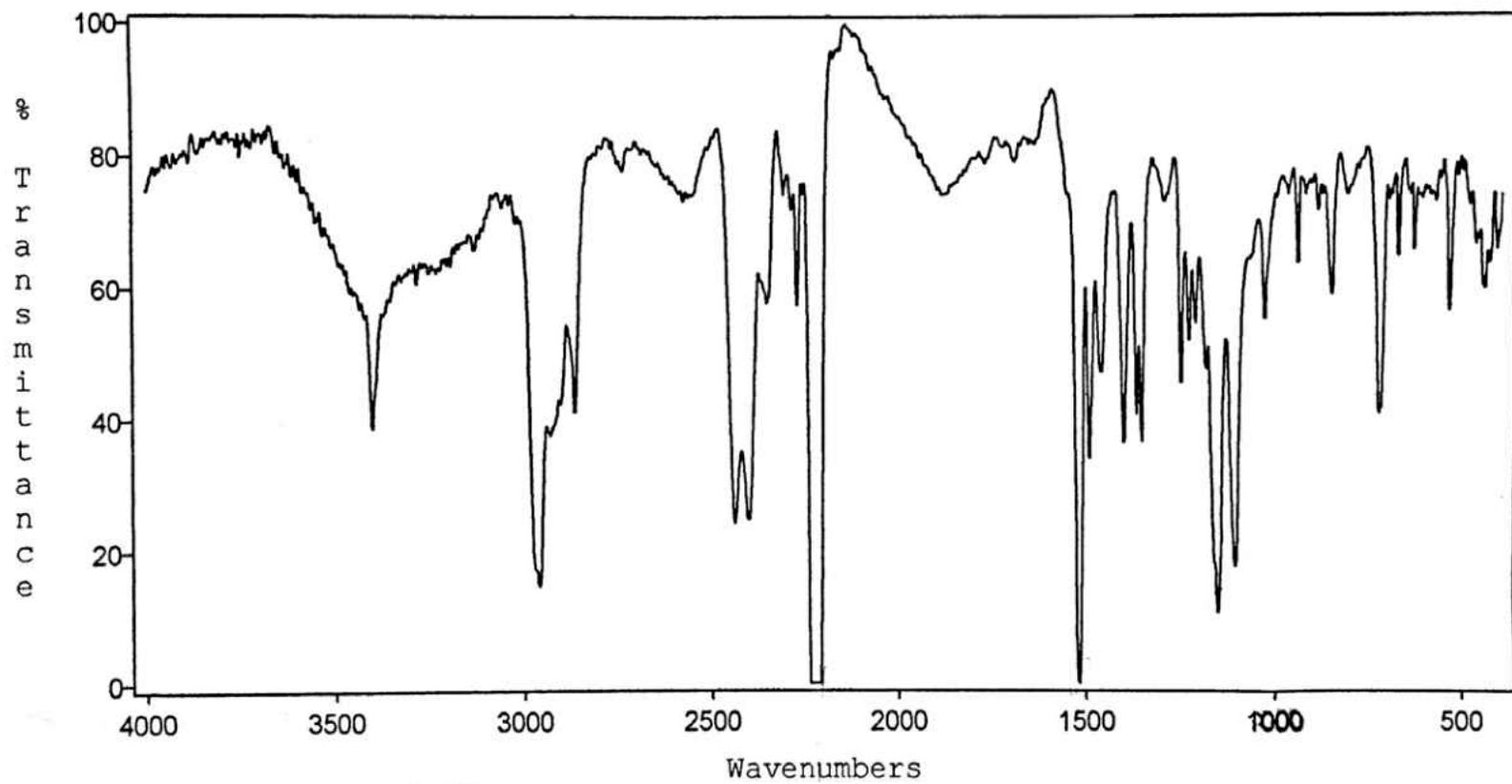


Figure 8 IR of $\text{KBp}^{t\text{-butyl}, 4\text{CN}}$

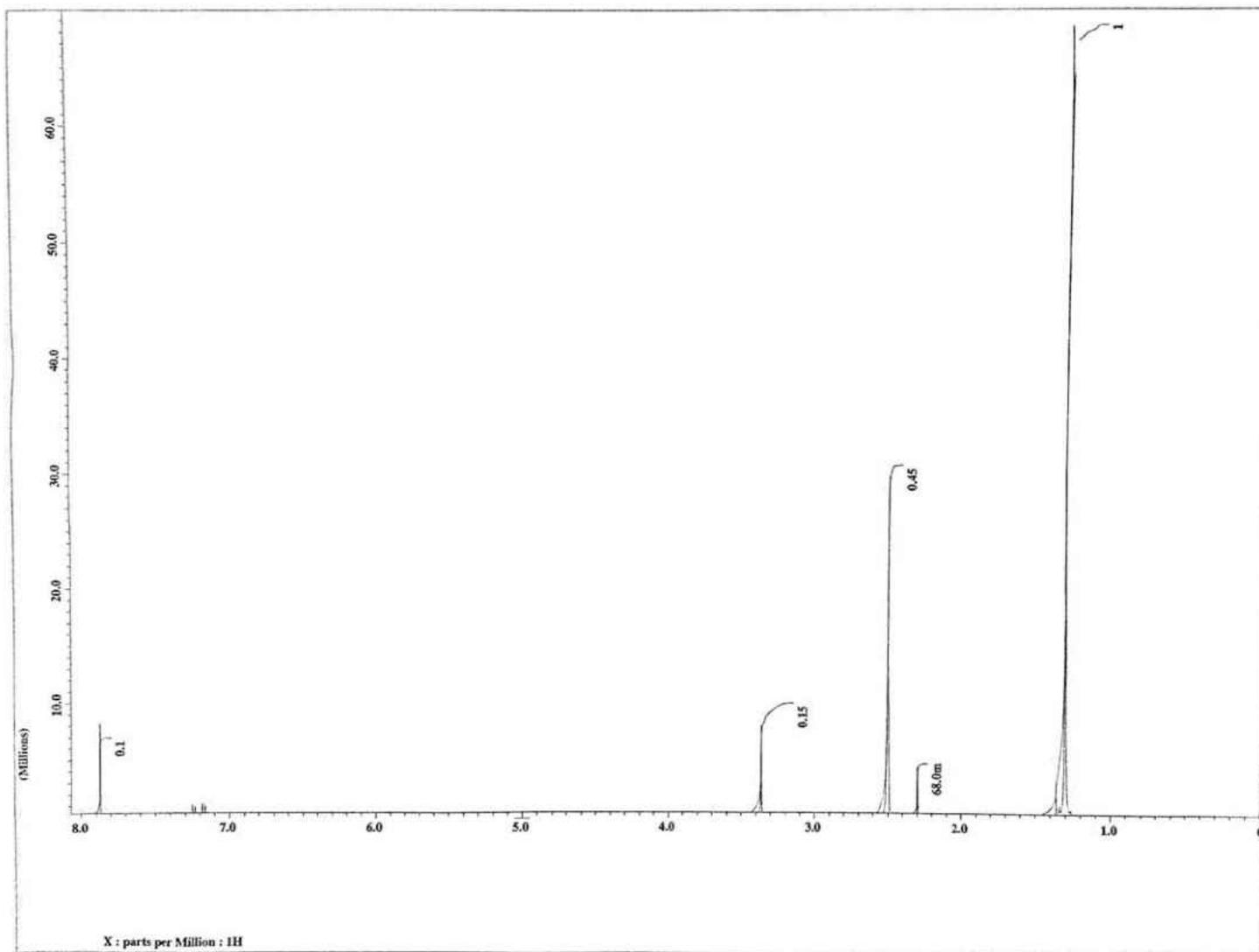


Figure 9 ^1H NMR of $\text{KBp}^{t\text{-Bu}, 4\text{CN}}$

To form the potassium dihydrobis(3-phenyl-4-cyanopolypyrazolyl)borate the mixture was heated to 140–150°C and stirred for one hour. The synthesis was followed as with the $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{K}$ ligand, no other steps were modified. The IR spectra in Figure 10 in conjunction with the NMR spectra in Figure 11 provide sufficient evidence to verify the identity of the end product. The IR spectra contains the characteristic B–H stretch at 2421.62 cm^{-1} and the cyano stretch at 2222.84 cm^{-1} . Multiplets at 7.35, 7.45, and 7.85 ppm with integrations of 0.11, 0.26, and 0.27, respectively, in the NMR spectra are characteristic of the phenyl substituent. The spectra also shows a singlet at 8.25 ppm with an integration of 0.14 that corresponds to the hydrogen on the number 5 position of the pyrazole. Additional peaks at 2.3, 7.15, and 7.25 ppm are due to small amounts of toluene still present from the last purification step. The DMSO-d_6 peak is also present at 2.5 ppm with a water peak at 3.35 ppm.

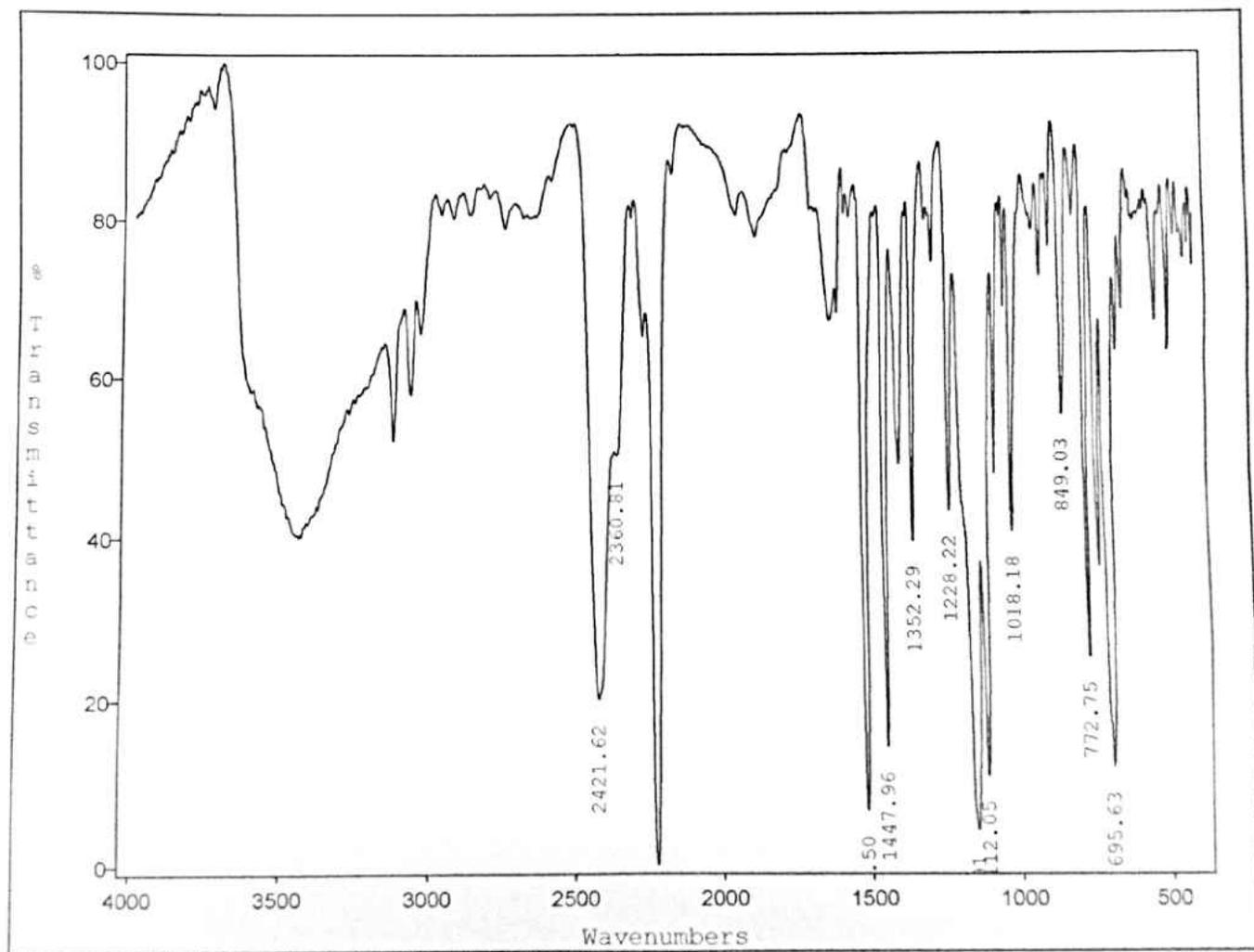
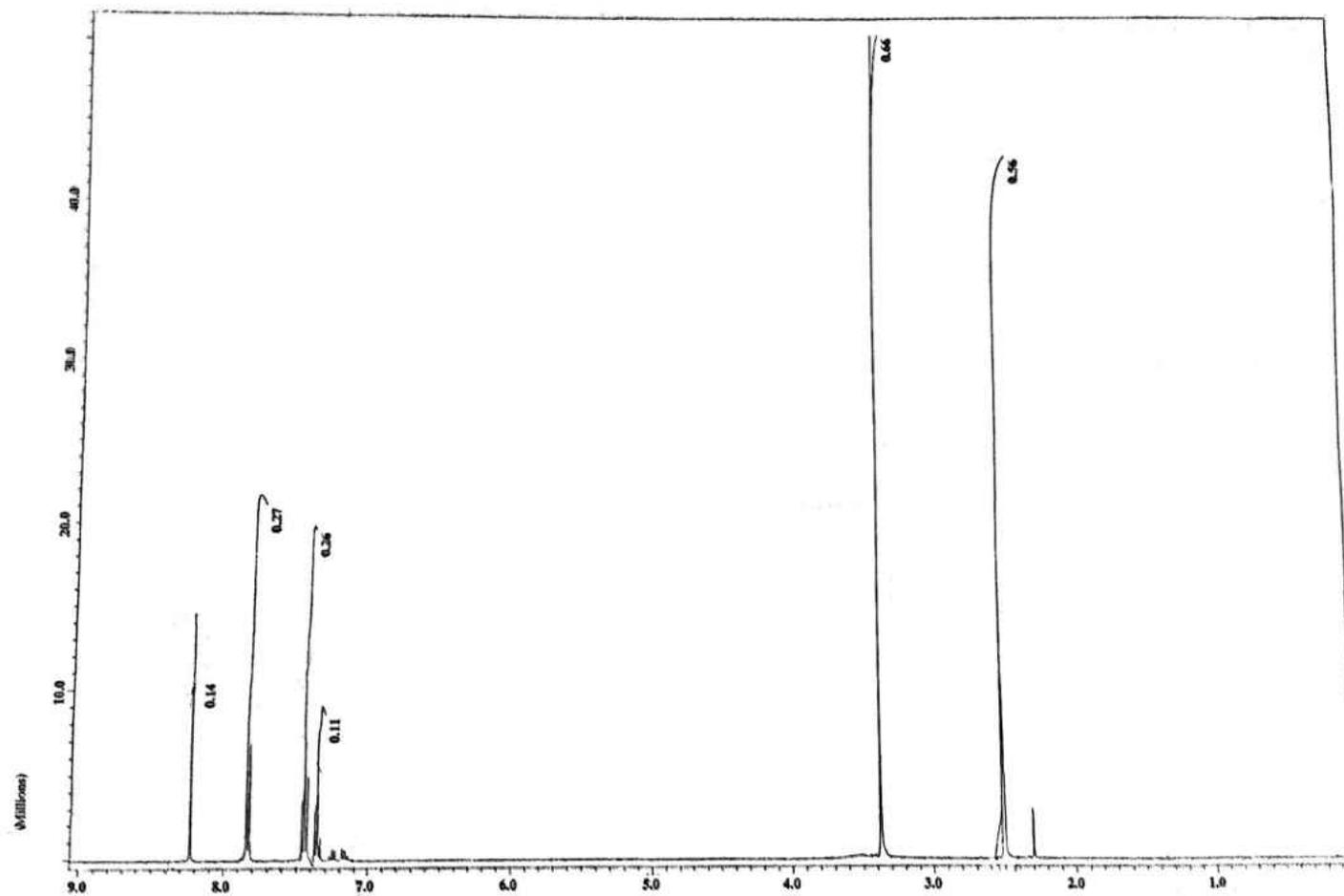


Figure 10 IR of $Bp^{Ph, 4CN}K$



X : parts per Million : HH

Figure 11 ^1H NMR of $\text{Bp}^{\text{Ph}}, ^4\text{CNK}$

Thallium Complexes

Further purification the ligand can be accomplished by binding it to the monovalent thallium cation. The formation of this complex will also allow x-ray quality crystals to be grown for the characterization of this ligand. The disubstituted cyanoscorpionate is synthesized as previously described and allowed to react with thallium nitrate in a 1:1 ratio as shown in Figure 12.

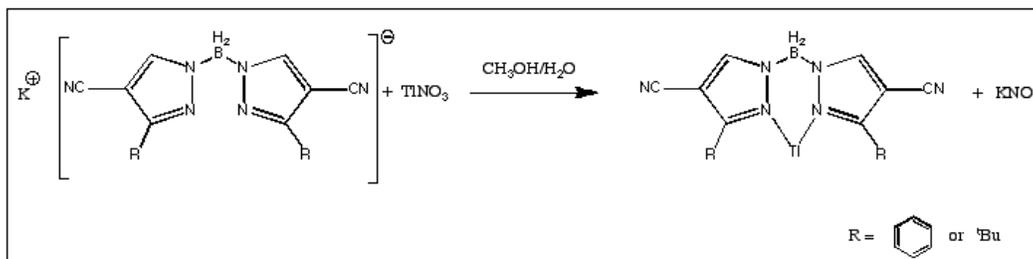


Figure 12 $\text{Bp}^{\text{R},4\text{CN}}\text{Tl}$ Synthesis

Thallium nitrate is soluble in water but insoluble in methanol. The solubility of cyanoscorpionate ligand prevents the reaction from taking place in pure water. This solubility conflict is resolved by dissolving the thallium nitrate in a beaker containing a 50/50 mixture of methanol and water. The solvent ratios are critical as we do not want either starting material to precipitate out of solution.

The $\text{Bp}^{t\text{-Bu},4\text{CN}}\text{Tl}$ was made by dissolving $\text{Bp}^{t\text{-Bu},4\text{CN}}\text{K}$ in a round bottom flask containing methanol. The thallium nitrate solution can then be added to the reaction flask and stirred for one hour. As the reaction proceeded, potassium nitrate precipitated out of solution.

After the reaction was complete, the solution was filtered to remove the insoluble potassium nitrate. The solvent is then removed under reduced pressure and the product is washed with water to remove any unreacted thallium nitrate. The solubilities of both $\text{Bp}^{t\text{-Bu},4\text{CN}}\text{K}$ and $\text{Bp}^{t\text{-Bu},4\text{CN}}\text{Tl}$ are identical so no attempt was made to remove any unreacted

Bp^{t-Bu, 4CN}K.

The IR spectrum in Figure 13 confirms the final thallium product retained the pyrazole ring, the cyano group, and the central boron with connecting hydrogen atoms, while the ¹HNMR spectrum in Figure 14 shows the presence of the tert-butyl group and the hydrogen on the number five carbon of the pyrazole. The IR spectrum has a peak around 2411 and 2362.9 cm⁻¹ that are characteristic of the B-H stretching frequencies. The cyano stretching frequency is present at 2225.81 cm⁻¹. The NMR spectrum shows a singlet peak at 1.3 ppm with an integration of 1 that corresponds to the tert-butyl group. The hydrogen on the number five carbon of the pyrazole is evident by the singlet peak at 7.9 ppm with an integration of 0.11. In addition to the characteristic peaks the spectrum also shows the presence of acetone at 2.9 ppm, DMSO-d₆ at 2.5 ppm, a water peak at 3.35 ppm, and an unidentified impurity at 3.17 ppm.

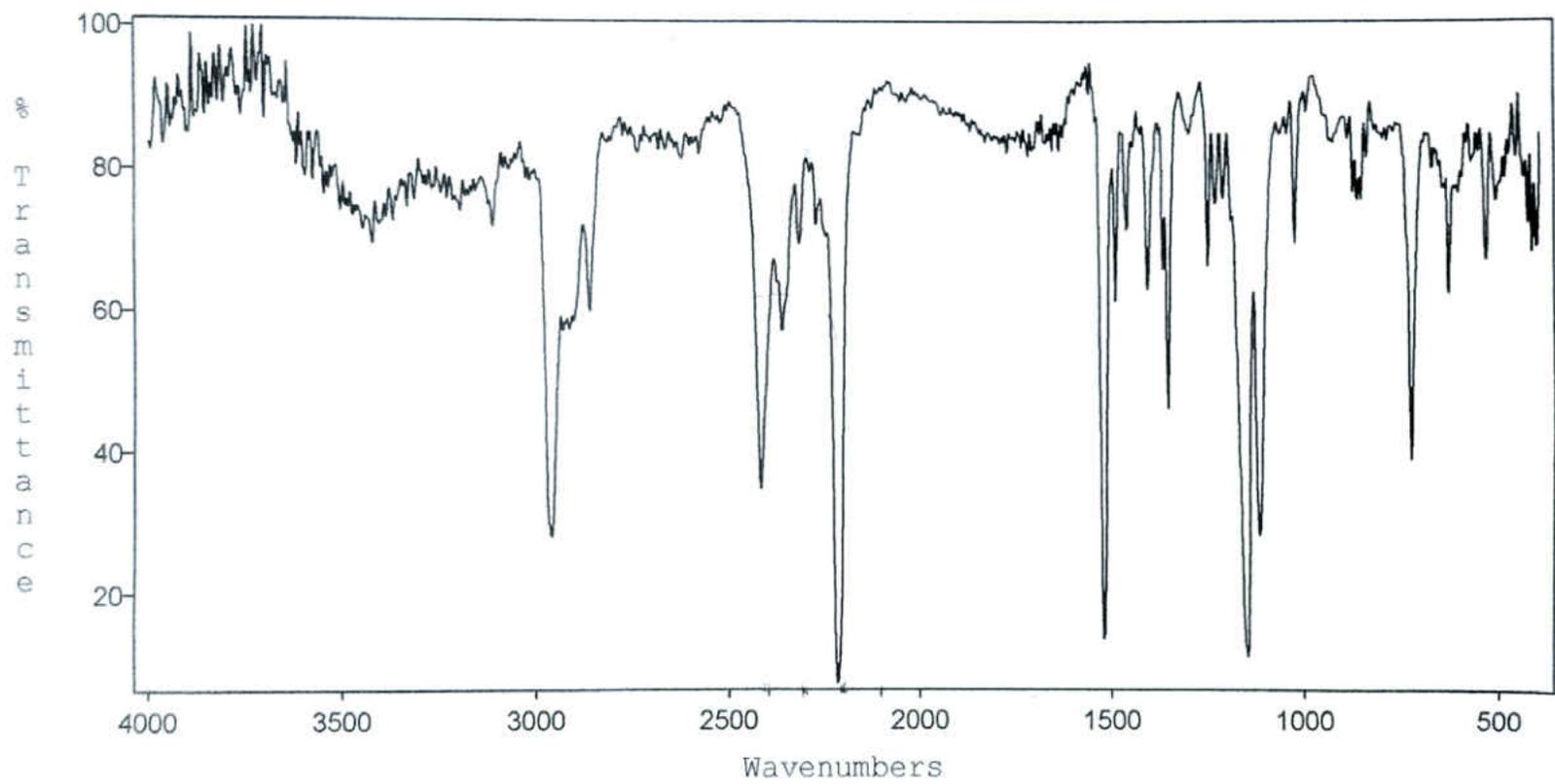


Figure 13 IR of Bp^{t-Bu, 4CN}T1

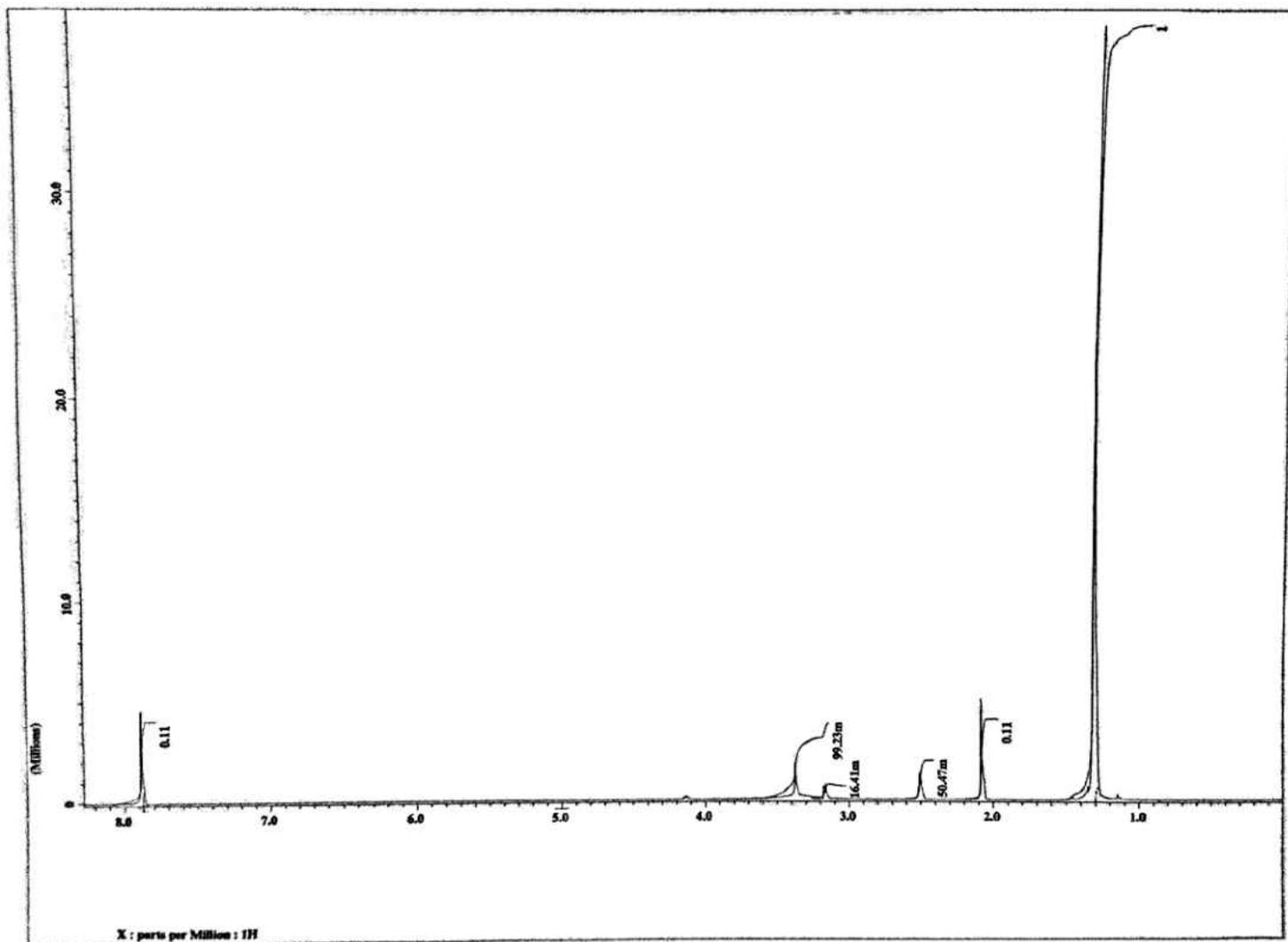


Figure 14 ^1H NMR of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$

The presence of acetone is accounted for because the NMR tube was washed with acetone. Evidently the tube was not allowed to dry completely before sample preparation. DMSO-d₆ was used as the solvent for the sample and the presence of water is understandable as it was used in the purification process.

To characterize the ligand x-ray quality crystals were grown by slow diffusion. Colorless crystals were obtained by layering a solution of Bp^{t-Bu,4CN}K in methanol over a saturated solution of TlNO₃ in a methanol/water solution. The x-ray crystal structure was determined and was indeed found to be Bp^{t-Bu,4CN}Tl. Table 1 compares the Bp^{t-Bu,4CN}Tl crystal data with that of comparable analogues. It is conclusive from the data

Table 1 Structural Comparison of Thallium Complexes

Bond	Bp^{t-Bu,4CN}Tl	Tp^{t-Bu,4CN}Tl¹	Bp^{t-Bu2}Tl¹⁴	BpTl¹⁵
Tl-N (Å)	2.788, 2.738	2.714 (Avg)	2.645, 2.632	2.799, 2.814
Tl-B (Å)	3.287	3.644	3.176	3.344
B-N (Å)	1.547, 1.546	1.544 (Avg)	1.645, 1.545	1.552 1.573
CN (Å)	1.142, 1.152	1.150	N/A	N/A
Tl-CN (Å)	3.093, 2.955	3.854 (Avg)	N/A	N/A
N-Tl-N (Degrees)	79.36	76.31	67.44	71.94
N-B-N (Degrees)	110.91	112.2	112.84	109.70
C-CN (Å)	178.80, 178.00	179.65 (Avg)	N/A	N/A

that the average Tl-N bond distance did increase from 2.639 Å (Bp^{t-Bu2}Tl) to 2.763 Å (Bp^{t-Bu,4CN}Tl), a 0.124 Å difference, with the addition of the cyano group on the number 4 carbon. Interestingly, the pocket effect may be decreasing the average N-Tl bond distance as it is 2.714 Å for the Tp^{t-Bu,4CN} complex. The Bp^{t-Bu,4CN}Tl crystal shows close contact between the cyano groups and neighboring thallium ions as the average distance is only

3.024 Å, 0.830 Å closer than that of $\text{Tp}^{\text{t-Bu},4\text{CN}} \text{Tl}$. Figures 15 and Figure 16 are ORTEP Mercury drawings from the crystal data and show the overall structure of the thallium complex while Figure 17, also an ORTEP Mercury drawing, shows the close contact between cyano nitrogen atoms, colored blue, and neighboring thallium ions colored magenta.

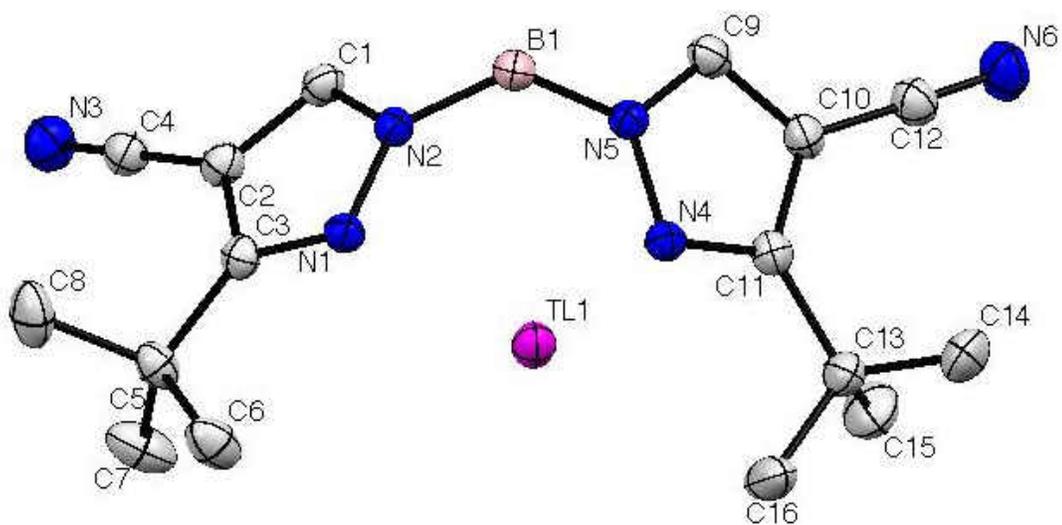


Figure 15 ORTEP Mercury drawing of $\text{Bp}^{t\text{-Bu}, 4\text{CN}}\text{Tl}$. Hydrogen atoms have been omitted for clarity.

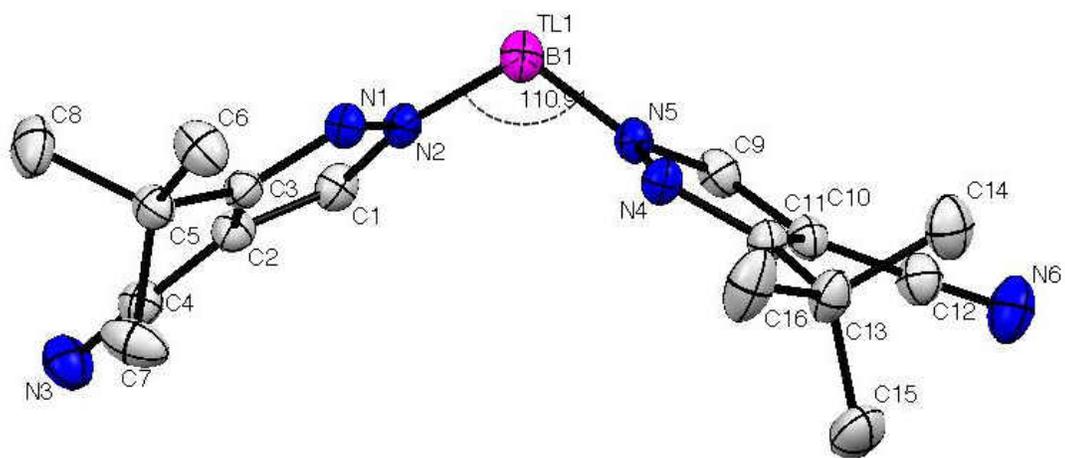


Figure 16 ORTEP Mercury drawing of $Bp^{t-Bu, 4CN}Tl$ bottom view. Bottom view shows the N2-B1-N5 bond angle of 110.91° by looking through TL1 and B1. Hydrogen atoms have been omitted for clarity.

Because the $\text{Bp}^{\text{t-Bu},4\text{CN}}\text{Tl}$ complex was easily crystallized by slow diffusion, the same process was used in attempts to make $\text{Bp}^{\text{Ph},4\text{CN}}\text{Tl}$ crystals. The crystals grown were long needles that have yet to be analyzed by x-ray diffraction. The IR spectra in Figure 18 and the NMR spectra in Figure 19 of $\text{Bp}^{\text{Ph},4\text{CN}}\text{Tl}$ contain all the characteristic peaks for the $\text{Bp}^{\text{Ph},4\text{CN}}$ ligand. The IR spectra of these crystals does indicate the presence of the boron atom as there are B-H stretches at 2465.16 and 2405.80 cm^{-1} . The cyano peak is also present at 2225.25 cm^{-1} . The $^1\text{HNMR}$ data show a doublet at 7.85 ppm with an integration of 0.3 beside multiplets at 7.45 and 7.35 ppm with integrations of 0.3 and 0.15, respectively. This grouping of peaks is indicative of the phenyl ring and the singlet at 8.25 ppm with an integration of 0.15 shows the presence of the hydrogen of the number 5 position of the pyrazole ring. The solvent of DMSO-d_6 at 2.5 ppm was once again accompanied by a water peak at 3.3-3.4 ppm.

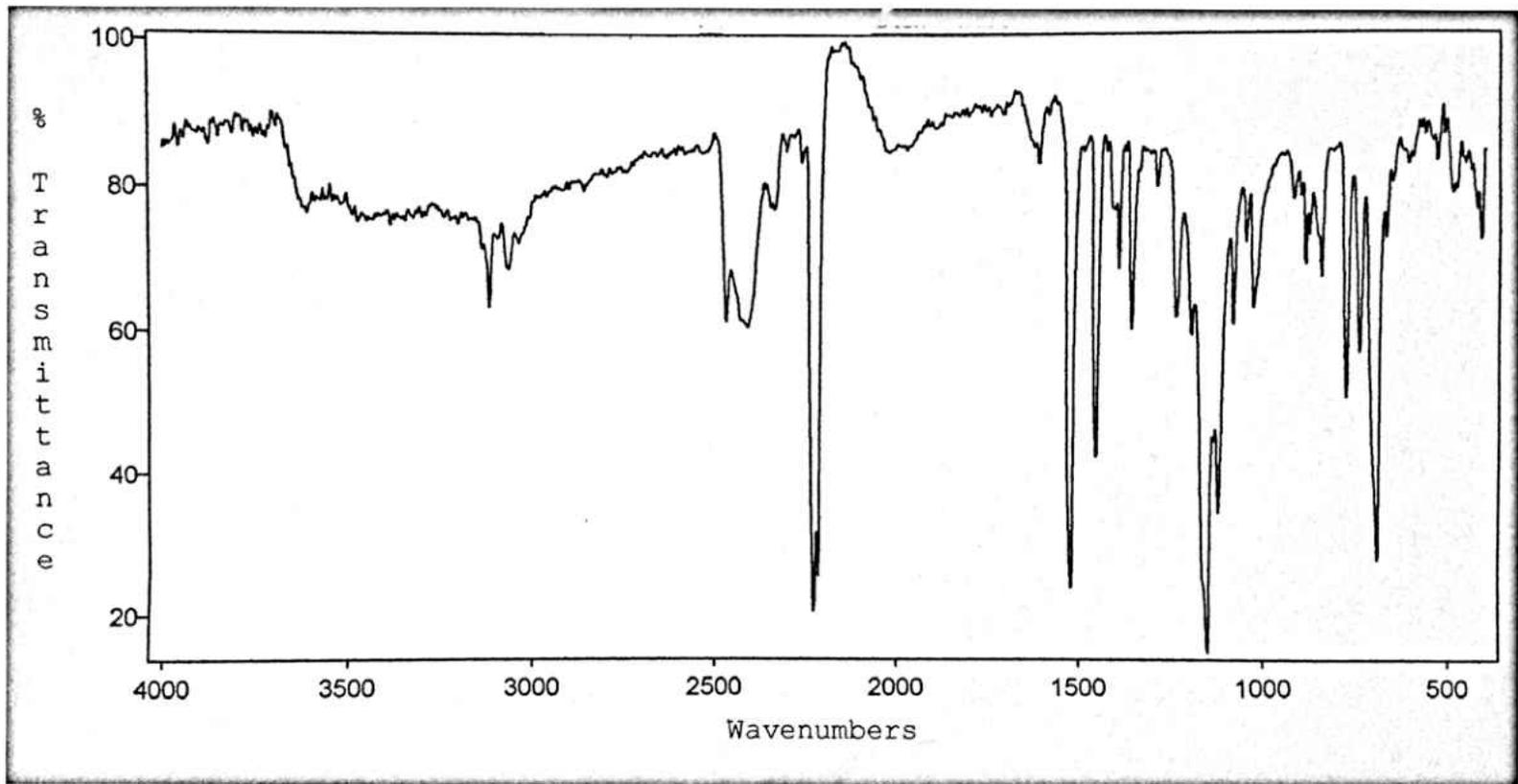


Figure 18 IR of $Bp^{Ph, 4CN}Tl$

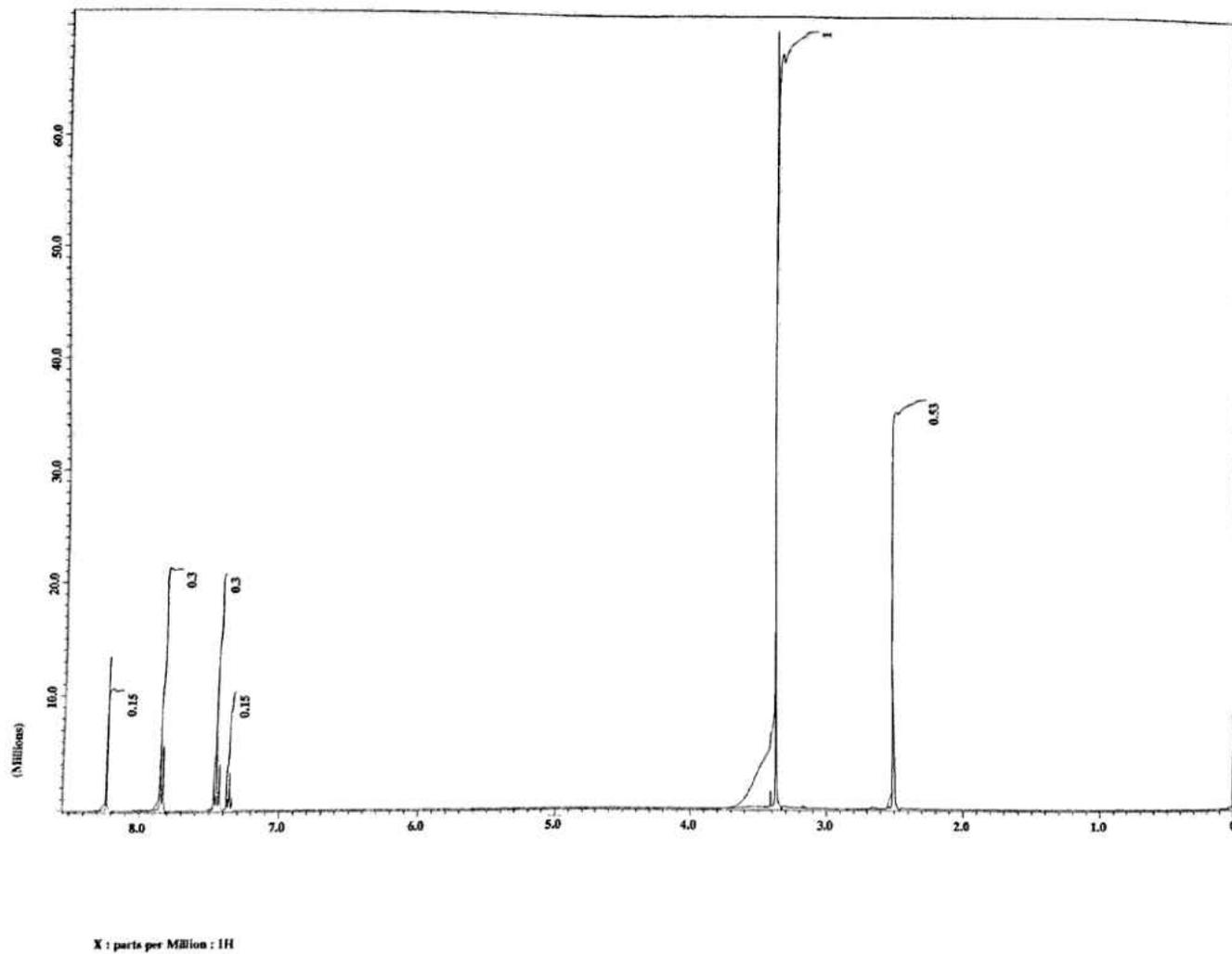


Figure 19 ^1H NMR of $\text{Bp}^{\text{Ph}, 4\text{CN}}\text{Tl}$

In conclusion, our attempt to prepare the bidentate $\text{Bp}^{\text{t-Bu},4\text{CN}}$ ligand was successful. The formation of this ligand will allow further study of the cyano functional group and its electronic effects brought about in this class of ligands. As in theory, replacing the potassium ion with the monovalent thallium ion resulted in a product that was easily crystallized. The crystals were analyzed with an x-ray diffractometer and the product was structurally characterized.

As predicted, the cyano group did lengthen the thallium-nitrogen bond distance when compared to the $\text{Bp}^{\text{t-Bu}_2}\text{Tl}$. Unexpectedly, the x-ray crystallographic data also show that the nitrogen-thallium bond distance of the $\text{Bp}^{\text{t-Bu},4\text{CN}}$ is greater than that of the tridentate version. This effect was not anticipated as we were using one less bulky group. A possible explanation for this result is that the presence of a third pyrazole group is creating a "pocket". This pocket effect is stabilizing the complex and allowing the thallium ion to set in closer. The structural data also show that there is close contacts between the cyano nitrogen atoms and neighboring thallium ions. These close contacts indicate the ligands potential to form coordination polymers.

CHAPTER 3

TRANSITION METAL COMPLEXES

Polypyrazolylborates will generally form coordination complexes with transition metals relatively easily.⁷ Depending on the charge and the geometry of the transition metal, a 1:1 or a 2:1 ligand-to-metal ratio is possible. Both the $\text{Tp}^{\text{t-Bu}, 4\text{CN}}$ and $\text{Bp}^{\text{Ph}, 4\text{CN}}$ ligands have been found to form coordination complexes with copper and cobalt.^{1,3} Forming these complexes with our $\text{Bp}^{\text{t-Bu}, 4\text{CN}}$ ligand would provide further insight as to how the number of pyrazoles in combination with cyano and *tert*-butyl substituents affect the metal ligand complexes. In addition to the traditional complex, a unique configuration of $\text{Tp}^{\text{t-Bu}, 4\text{CN}}$ ligand has been successfully coordinated to divalent cobalt, manganese, and nickel ions. In this particular coordination environment the ligand is chelated to the metal through only the cyano group. It appears as though the formation of this type of coordination complex is dependent on the crystal structure of the potassium complex.¹¹ Because $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{K}$ has yet to be structurally characterized, coordination through the cyano group was not attempted. The $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{Tl}$ crystal structure shows close contact between the nitrogen atoms on the cyano groups and adjacent metal centers. This could indicate that the cyanide group on our new ligand has the ability to coordinate to another metal center as was predicted. We hope to observe the same cyano metal interaction for the copper as we did for the thallium complex. The cobalt complex was also attempted, but the desired product has yet to be isolated.

The (Bp^{t-Bu,4CN})₂Cu Complex

Two methods were tried in attempts to create a 2:1 ligand-to-metal copper complex. The first method uses copper nitrate as the starting material and the second method uses copper chloride. There appeared to be a significant difference between the final products of the two methods.

Method A

The first method uses copper nitrate as the starting material. Both the KBp^{t-Bu,4CN} ligand and the copper nitrate were separately dissolved in tetrahydrofuran. The ligand-to-metal ratio was 2:1 as illustrated in Figure 20. The product is a sandwich complex. The two solutions were mixed and stirred for an hour. There was a drastic change from light blue to deep blue when the solutions were combined. As time progressed the color began to lighten from deep blue to a light blue. A precipitate, potassium nitrate, was observed as the color lightened. The final

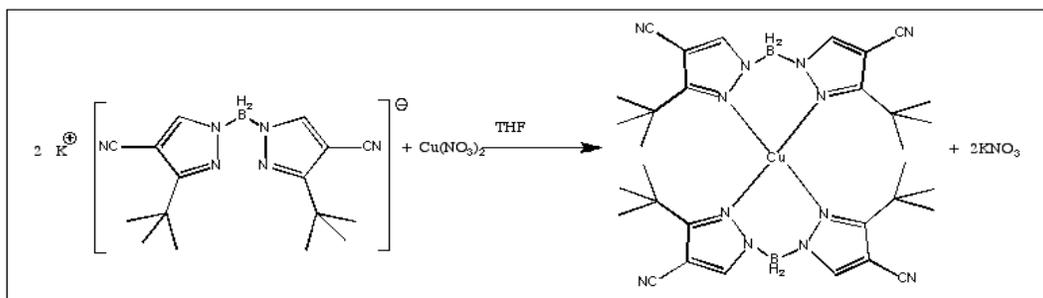


Figure 20 Synthesis of (Bp^{t-Bu,4CN})₂Cu

color of the solution was light green. The mixture was then filtered to remove the insoluble material and left a clear green solution. The solvent was then removed from the green solution by roto-evaporation under reduced pressure, and a blue/green colored oil remained. Then the product was dissolved in a minimal amount of tetrahydrofuran followed by 25 mL of methylene chloride. Upon addition of the methylene chloride, a green blue

precipitate precipitated out of solution. The mixture was filtered and the solid was discarded. The remaining solution was light blue. The solvent was then removed under reduced pressure to leave a light blue precipitate. The IR spectra in Figure 21 reveals that the product does have the B-H stretches at 2430.74 and 2374.63 cm^{-1} and a cyano stretch at 2227.39 cm^{-1} .

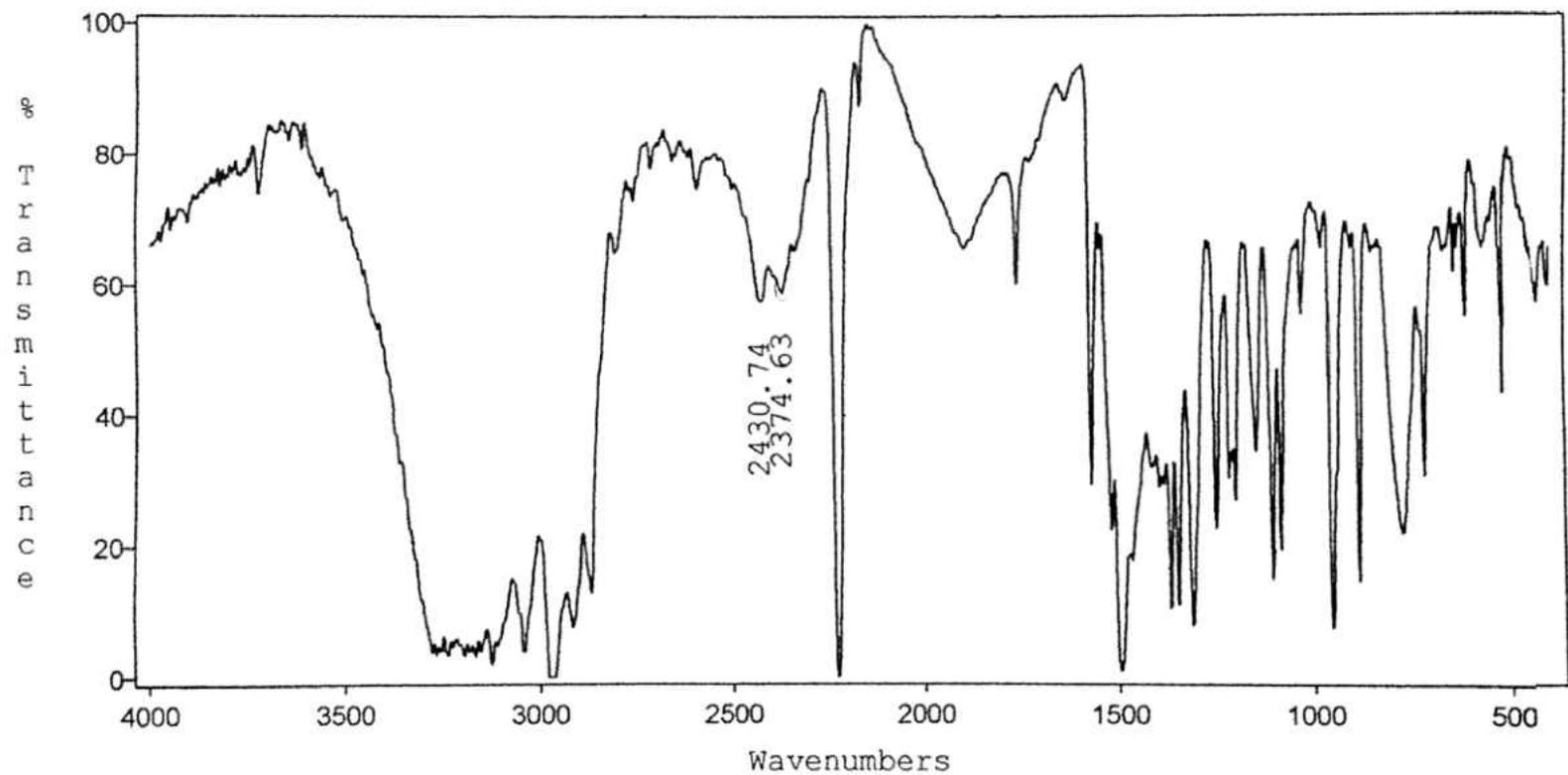


Figure 21 IR of $(\text{Bp}^{\text{t-Bu}, 4\text{CN}})_2\text{Cu}$ Method A

Colorless crystals were grown by slow evaporation with 50/50 THF/Toluene. The crystals produced did not retain the B-H stretch in its IR spectrum as shown in Figure 22. The characteristic cyano stretch at 2235.68 cm^{-1} was present. Due to the color and spectral data it appears that the crystals are of the pyrazole and not the cyanoscorpionate complex. The presence of these crystals could indicate decomposition of the complex. X-ray quality crystals of the complex have yet to be isolated. Because we do not have the crystal structure, it is not possible at this point to know if the complex is truly 2:1. Further research is needed.

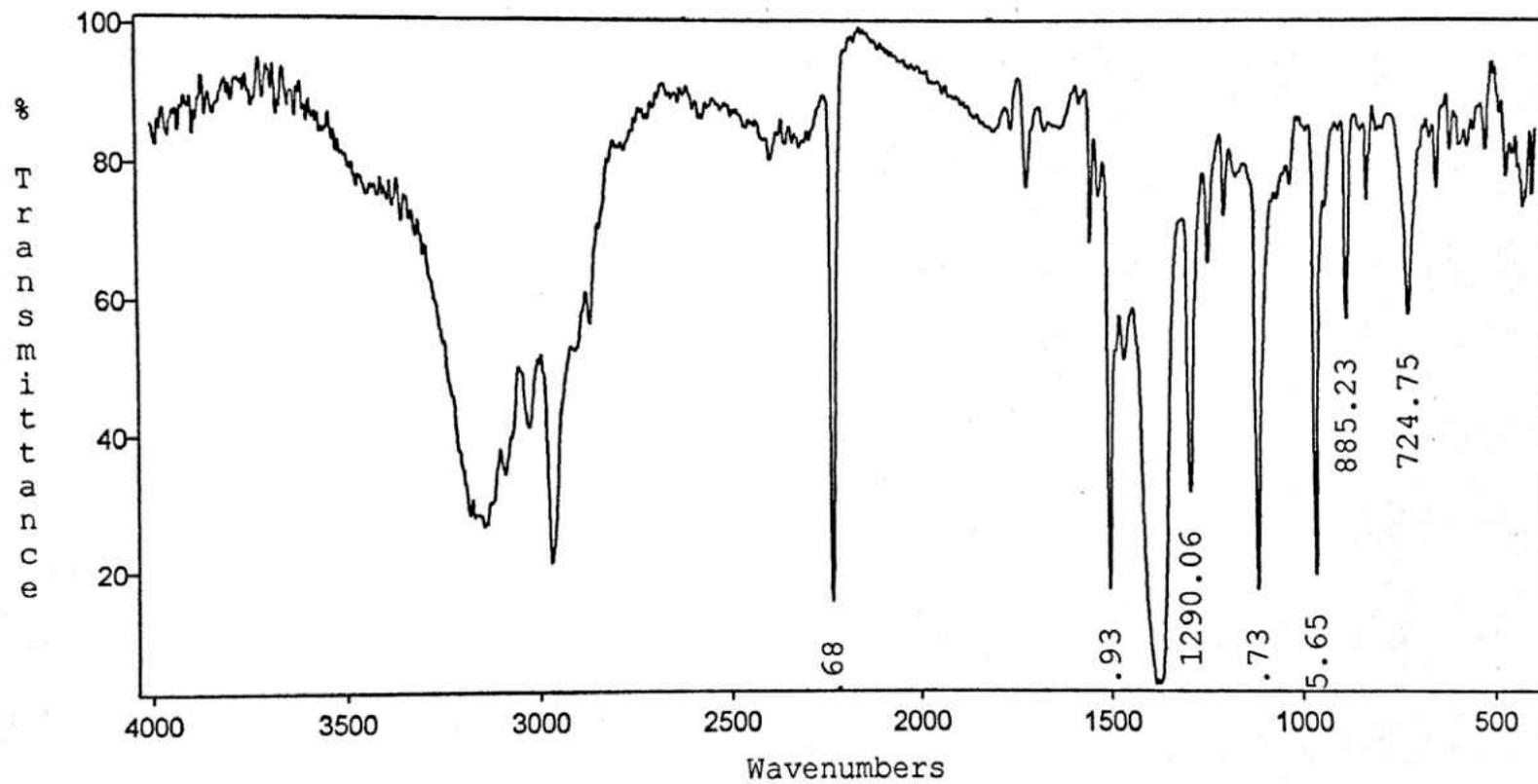


Figure 22 IR of $(\text{Bp}^{\text{t-Bu,4CN}})_2\text{Cu}$ Flat Crystals from Method A

Method B

The second method involved dissolving $\text{KBp}^{\text{t-Bu},4\text{CN}}$ in methanol and adding it to a solution of copper chloride in methanol. The ligand-to-metal ratio was 2:1. The color changed dramatically from a light green to a dark green/black. As the solution was stirred it slowly lightened in color. In addition to the color change a white precipitate was observed. After an hour the contents of the flask were filtered. Once the precipitate was filtered out of solution, the remaining solution was clear and yellow, nearly colorless. The solvent was removed by roto-evaporation leaving behind a very light yellow solid almost colorless. Upon dissolving the solid in tetrahydrofuran the solution immediately turned green with the formation of a red/brown precipitate. The same precipitate was also observed upon redissolving the light yellow solid in methanol. Once filtered the precipitate was no longer soluble in any available solvents. Why the red/brown precipitate is produced upon redissolving in methanol is unclear. The precipitate could contain a coligand that is preventing it from being redissolved. Another possibility is that the complex is polymerizing. Interestingly, if the red/brown precipitate is allowed to remain in THF for several weeks, it slowly dissolves forming a green solution. There seems to be a point at which this concentration reaches a critical level where the solvated product becomes insoluble and crashes out leaving a light green insoluble material. The IR spectra of the red/brown precipitate in Figure 23 shows that the precipitate has the cyano characteristic peak at 2236.69 cm^{-1} . The spectra also show a broad stretch at 2400.1 cm^{-1} . While this peak is in the region of the characteristic B-H stretch, it is too broad to confirm it as such.

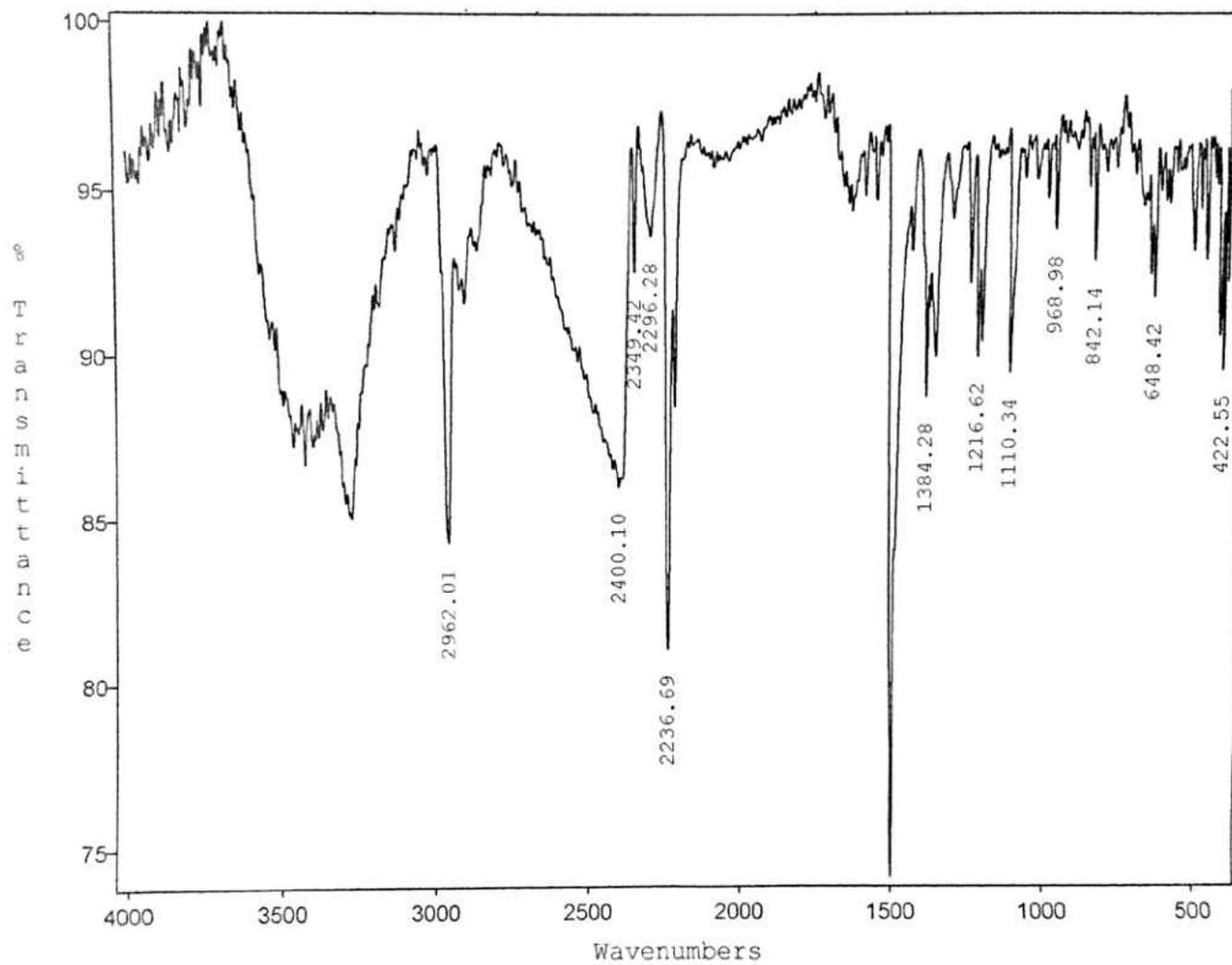


Figure 23 IR of Red/Brown Precipitate from Method B

The solvent was then removed from the remaining green solution to leave a green solid. Interestingly, the green product was soluble in diethyl ether. The IR data in Figure 24 show that the green product has the characteristic cyano stretch at about 2228.8 cm^{-1} ; however, still no B-H stretch was found. Crystalline material has been produced but no isolated x-ray quality crystals have been grown. Because no crystal structure has been obtained, it is difficult to tell exactly what the green product is. Short contact between the boron and another atom may be interfering with the observation of the B-H stretch. Another possibility for the absence of the stretch is that somewhere in the procedure the $\text{Bp}^{\text{t-}}$ ^{Bu, 4CN} ligand decomposes. Generally scorpionate transition metal complexes have been quite stable, but it has been known that solutions of $(\text{Bp})_2\text{Cu}$ exhibit an increased sensitivity toward photodecomposition with the introduction of benzophenone.¹⁶ While benzophenone was used in drying the toluene for pyrazole synthesis, it is unlikely that it made its way into the copper complex. Further research is needed to determine the structure of the product.

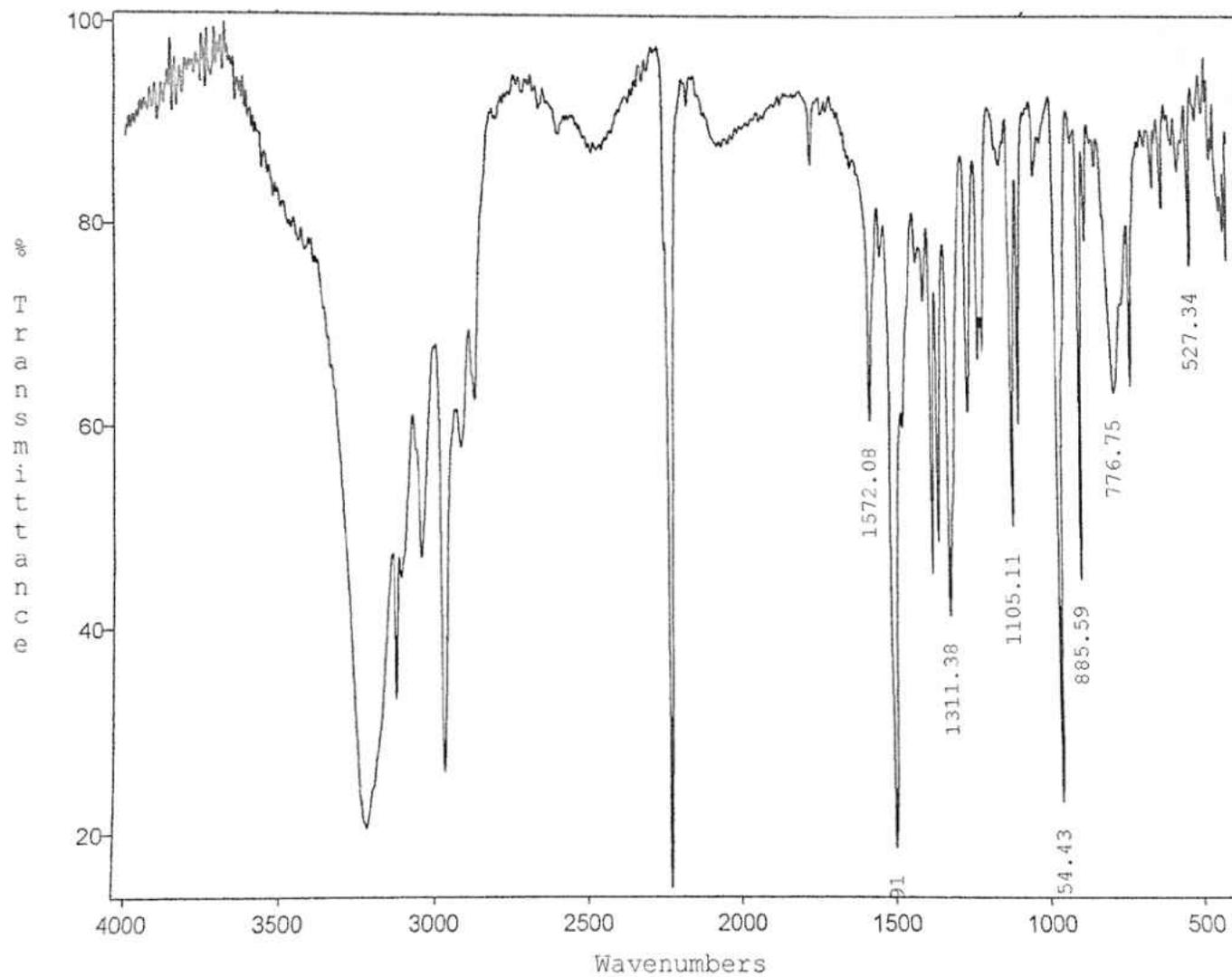


Figure 24 IR of Soluble Green Precipitate from Method B

In conclusion, the synthesis of $(\text{Bp}^{\text{t-Bu},4\text{CN}})_2\text{Cu}$ was attempted using two different starting materials. The first starting material, copper nitrate, appears to be more successful in acquiring the desired product than using copper chloride. The process did however result in a poor yield of only 20% assuming a 2:1 complex. The IR spectrum did show the characteristic B-H stretch at 2430.74 and 2374.63 cm^{-1} along with the cyanide stretch at 2227.39 cm^{-1} .

The second starting material, copper chloride, did not produce the desired product as indicated by the lack of the B-H stretch in the IR spectrum of the two materials. It is possible that that the boron is involved in some sort of close contact that is hiding the stretch. A second possibility is that at some point in the procedure the ligand is decomposing. A possible indication of decomposition is upon the addition of tetrahydrofuran, as it forms a red/brown precipitate that no longer retains its solubility in methanol. The green product in Figure 24 is clearly not starting material as it is readily soluble in diethyl ether. $\text{Bp}^{\text{t-butyl},4\text{CN}}\text{K}$ is not soluble in diethyl ether and Copper chloride is only slightly soluble in the diethyl ether. Due to the slow progress in isolating an x-ray quality crystal, the actual structure is unknown at this time. Because the identity of the final product is not yet known, the percent yield cannot be calculated. It is quite obvious that the two methods produce different products, as the second complex is insoluble in diethyl ether. Isolated crystals have yet to be grown. At this point it is inconclusive whether the complex is truly a 2:1 or a 1:1 ligand/metal ratio. Further research is needed.

Further Research

In addition to the work that has been done, there is much more that we would like to do with this ligand. The crystallization of the potassium complex was not accomplished. A crystalline material was produced through slow evaporation with a 50/50 tetrahydrofuran/toluene solvent but no good quality isolated crystals were grown. It has been reported by Bullinger and Eichhorn that crystals of the potassium $\text{Tp}^{\text{t-Bu}, 4\text{CN}}$ form have been successfully isolated using a methanol/toluene solution. In their article they describe some interesting structural arrangements within the crystal.¹¹ Early attempts of slow evaporation of the methanol/toluene solvent solution were not successful using our $\text{Bp}^{\text{t-Bu}, 4\text{CN}}$ ligand; however, there was noticeable improvement in the quality of the crystals produced. Further experimentation with solvent ratios and percent saturation may indeed provide us with isolated x-ray quality crystals. Comparison of the potassium $\text{Bp}^{\text{t-Bu}, 4\text{CN}}$ and $\text{Tp}^{\text{t-Bu}, 4\text{CN}}$ crystal structures would be of great interest.

As mentioned in previous chapters, Bullinger and Eichhorn were able to coordinate to the metal only through the nitrogen on the cyano group.¹¹ We would like to attempt to create this configuration with our $\text{Bp}^{\text{t-Bu}, 4\text{CN}}$ product also.

Experimental

General Experimental

Except where otherwise stated all chemical reagents and solvents were used as received from the manufacturer. Dry toluene was dried under sodium/benzophenone and distilled. Solvents were removed from solution using a BUCHI SWITZERLAND Rotavapor RII. Glassware was cleaned by soaking

in a KOH/isopropanol/water base bath, then rinsed with de-ionized water and dried over night in at 90°C in a Fisher Scientific Isotemp Oven. All weight measurements were performed using a METTLER TOLEDO CLASSIC Plus PB403-S/FACT laboratory balance. IR spectroscopy samples were prepared by pressing in potassium bromide pellets. IR spectra were obtained using a Mattison Instruments Genesis II FTIR spectrophotometer. NMR spectrographs were obtained by using an Oxford NMR AS400 spectrophotometer. X-ray crystallographic data were obtained from Wichita State University's Department of Chemistry, where the crystals were sent and analyzed using a Bruker Kappa-Apex-II area-detector diffractometer with the Bruker Apex2 suite (v2.0-2).

Synthesis of Hpz^{t-Bu, 4CN}

A solution containing 2.816g (0.0703 mol) of 60% sodium hydride dispersed in mineral oil and 150 mL dry toluene was cooled in an ice bath. *Tert*-butyl-cyanoacetate was added drop wise in the amount of 10g (0.0709 mol) to the toluene/sodium hydride mixture. Upon addition of the *tert*-butyl-cyanoacetate, hydrogen gas was produced. The solution was allowed to stir overnight under nitrogen. Then 9.884g (0.0703 mol) of trimethylacetyl chloride was added drop wise to the reaction flask. The contents of the reaction flask were then stirred overnight under nitrogen.

The solution was then washed with 100 mL of 0.2 M aqueous sodium hydroxide three times in a separatory funnel. Between washings the aqueous layers were collected and combined. The resulting aqueous solution was then washed once with 100 mL of diethyl ether. The pH of the aqueous solution was then adjusted to ~1 using half diluted hydrochloric acid. Upon addition of the acid, a white precipitate was formed. The mixture was then washed with 100 mL of diethyl ether three more times in a

separatory funnel. The organic layers were separated between washings and then combined. The combined organic layers were then passed through a filter containing anhydrous magnesium sulfate. The solvent was then evaporated under reduced pressure to leave 6.793g (0.0277 mol) of product, a 39.4% yield. The product was then dissolved in 150 mL of dry toluene and 0.527g (0.00277 mol) of p-toluenesulfonic acid was added. The reaction flask was connected to a reflux column. The solution was allowed to boil at reflux over night.

The solution was then filtered and the solvent was evaporated under reduced pressure to leave 4.851g (0.0335 mol) of product. The product was then re-dissolved in 150 mL of dry toluene and 3.635g (0.0277 mol) of N,N-Dimethylformamide dimethyl acetyl was added to the solution. The mixture was then stirred overnight under nitrogen.

The solvent was then evaporated under reduced pressure and the crude product was then dissolved in a minimal amount of methylene chloride. The solution was then chromatographed using a silica gel column with methylene chloride as the mobile phase. The desired product had the lowest retention time and was the first to come off. The solvent was evaporated under reduced pressure to give 3.67g (0.0204 mol) of product. The solvent was removed by evaporation under reduced pressure. The product was then dissolved in 100 mL of methanol. Hydrazine monohydrate was then added to the solution in the amount of 2.039g (0.0408 mol). The solution was stirred overnight.

The solvent was then removed by evaporation under reduced pressure and the residue was dissolved in a minimal amount of 50/50 ethyl acetate/hexanes. The product was then chromatographed using a silica gel column with 50/50 ethyl acetate/hexanes as the mobile phase. The pyrazole had the lowest retention time and was the first to be removed from the

column. The solvent was removed under reduced pressure to give a 98.38% yield of 2.989g (0.0201 mol) of 4-cyano-3-tert-butylpyrazol. Infrared spectroscopy shows a peak corresponding to the CN stretch at approximately 2226.93 cm^{-1} . ^1H NMR spectroscopy showed the tert-butyl peak at about 1.5 ppm with an integration of 1 and the hydrogen on the 5 carbon at about 7.85 ppm with an integration of 0.1.

Synthesis of $\text{Hpz}^{\text{Ph}, 4\text{CN}}$

Refer to synthesis of $\text{Hpz}^{\text{t-Bu}, 4\text{CN}}$. With the exception of substituting benzoyl chloride for trimethylacetyl chloride all steps were identical. A 17.78% yield was obtained using the modified Tupper and Bray synthesis. Infrared spectroscopy shows a peak corresponding to the CN stretch at approximately 2226.93 cm^{-1} . ^1H NMR spectroscopy showed the phenyl peaks as multiplets at 7.5 and 7.55 ppm with a doublet at 7.89 ppm. The hydrogen on the 5 carbon is shown as a singlet at 8.88 ppm.

Synthesis of $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{K}$

A portion of 4-cyano-3-tert-butylpyrazole (3.000 g, 20.13 mmol) was added to 0.544 g (0.0101 mol) of potassium borohydride in a 100 mL round bottom flask equipped with a water cooled condenser. The mixture was then heated to $130\text{ }^{\circ}\text{C}$ and stirred for one hour. Hydrogen bubbles were produced as the pyrazole melted. After about 30 minutes the mixture solidified. The residue was then dissolved in acetonitrile and filtered to remove any excess KBH_4 . The solvent was then removed under reduced pressure. The product was then dissolved in a minimal amount of THF followed by enough Toluene to cause the $\text{KBp}^{\text{t-butyl}, 4\text{CN}}$ to precipitate. The solution was then boiled in toluene to further remove any unreacted pyrazole. The solution was then filtered and the $\text{KBp}^{\text{t-butyl}, 4\text{CN}}$ was collected

and allowed to dry. Upon drying the product was a fine white powder. X-ray quality crystals have not yet been successfully grown. Infrared spectroscopy shows peaks corresponding to the B-H stretch at approximately 2436 and 2403 cm^{-1} . The CN stretch is observed at approximately 2225 cm^{-1} . NMR spectroscopy showed the tert-butyl peak at about 1.3 ppm with an integration of 1 and the hydrogen on the 5 carbon at about 7.88 ppm with an integration of 0.1.

Synthesis of $\text{Bp}^{\text{Ph}, 4\text{CN}}\text{K}$

The synthetic procedure was modified by the change to $\text{Hpz}^{\text{Ph}, 4\text{CN}}$ as the pyrazole starting material and the increase to 140–150 $^{\circ}\text{C}$ in the reaction temperature. All other procedures were followed in the same manner as was the $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{K}$ complex. A 75.13% yield was obtained. Infrared spectroscopy shows a peak corresponding to the B-H stretch at 2421.62 cm^{-1} . The CN stretch is observed at approximately 2222.84 cm^{-1} . ^1H NMR spectroscopy showed the phenyl peaks as multiplets at 7.35, 7.45, and 7.85 ppm with integrations of .11, 0.26, and 0.27, respectively. The hydrogen on the 5 carbon is present as a singlet at about 8.25 ppm with an integration of 0.14.

Synthesis of $\text{Bp}^{\text{t-Bu}, 4\text{CN}}\text{Tl}$

The ligand was then coordinated to thallium for the purpose of purification and characterization. A solution containing 0.200 g (.000574 mol) of $\text{KBp}^{\text{t-butyl}, 4\text{CN}}$ dissolved in methanol was added to a solution of 0.153 g (.000574 mol) of TlNO_3 dissolved in 50/50 H_2O /methanol. The combined solution was stirred for one hour. Upon stirring the clear colorless solution became cloudy. The solvent was then removed under reduced pressure and washed with water to dissolve any nitrates. The product was then filtered out of solution and allowed to dry. X-ray quality crystals

were grown by slow diffusion. A 1/20 saturated solution of $\text{KBp}^{t\text{-butyl}, 4\text{CN}}$ in methanol was layered over a saturated solution of TlNO_3 in 50/50 H_2O /methanol. The two layers were then allowed to diffuse over a span of several weeks. Infrared spectroscopy shows peaks corresponding to the B-H stretch at approximately 2411 and 2363 cm^{-1} . The CN stretch is observed at approximately 2226 cm^{-1} . NMR spectroscopy showed the tert-butyl peak at about 1.3 ppm with an integration of 1 and the hydrogen on the 5 carbon at about 7.9 ppm with an integration of 0.11.

Growth of $\text{Bp}^{Ph, 4\text{CN}}\text{Tl}$ Crystals

A saturated solution of TlNO_3 in 50/50 methanol/water was added to a test tube in the amount of 2 ml. A second solution containing 2 ml of a 0.0619M solution of $\text{Bp}^{Ph, 4\text{CN}}\text{K}$ in methanol was slowly layered onto the TlNO_3 solution. The test tube was sealed and the solutions were allowed to diffuse. Infrared spectroscopy shows peaks corresponding to the B-H stretch at 2465.16 and 2405.80 cm^{-1} . The CN stretch is observed at 2225.25 cm^{-1} . $^1\text{HNMR}$ spectroscopy shows phenyl peaks as a doublet at 7.85 ppm with an integration of 0.3 and multiplets at 7.45 and 7.35 ppm with integrations of 0.3 and 0.15, respectively. The hydrogen on the 5 carbon is shown as a singlet at 8.25 ppm with an integration of 0.15.

Transition Metal Complexes

Method A. A solution of 0.2 g (0.574 mmol) of $\text{KBp}^{t\text{-Bu}, 4\text{CN}}$ in 5 mL of tetrahydrofuran was added to a second solution containing 0.67 g (0.287 mmol) of copper nitrate in 5 mL of tetrahydrofuran. The solution was allowed to stir for one hour. Upon addition of the ligand the solution turned a dark blue. Within the first 10 minutes the solution lightened up

and a white precipitate of potassium nitrate was also observed. After 30 minutes the solution was colorless and still contained the white precipitate. After one hour the solution had a slight green hue and still contained the white precipitate. The solution was then filtered to remove the insoluble nitrate and left a light green solution. The solvent was then removed under reduced pressure to leave a green/blue oil. About 1 mL of THF was added to solvate the oil and then 25 mL of methylene chloride was added to precipitate out some impurity. The solution was then filtered to remove the green/blue precipitate. The final solution was a very light green/blue. The solvent was then removed to leave 0.102 g of a green/blue solid. The final yield was 20.8% assuming the final product is a sandwich complex. IR spectroscopy shows the B-H stretch at 2430.74 and 2374.63 cm^{-1} and the CN stretch at 2227.39 cm^{-1} . After slow evaporation from 50/50 THF/Toluene, flat colorless (possibly slightly green/blue) crystals were produced that no longer contained the B-H stretch but retained the CN stretch along with the pyrazole stretches. X-ray quality crystals have yet to be grown.

Method B. A solution of 0.206 g (0.591 mmol) of $\text{KBp}^{t\text{-Bu}, 4\text{CN}}$ in 5 mL of methanol was added to a second solution containing 0.051 g (0.296 mmol) copper chloride dihydrate in 5 mL of methanol. The mixture was allowed to stir for one hour. Upon addition of the ligand, the solution became a dark green color. Within the first 10 minutes the solution lightened up and a white precipitate of potassium chloride was also observed. After 30 minutes the solution was colorless and still contained the white precipitate. The solution was then filtered to remove the insoluble chloride and left a slightly pale yellow solution. The solvent was then removed under reduced pressure to leave a yellow/white precipitate. About

30 mL of tetrahydrofuran was added to dissolve the product. Upon addition a red/brown precipitate that was no longer soluble in methanol was formed. The solution was filtered to leave a light green solution. The solvent was removed to leave a green solid. IR spectroscopy only revealed cyanopyrazole stretches.

CHAPTER 4

CONCLUSIONS

With the introduction of cyanoscorpionates Trofimenko expanded the potential uses for scorpionate ligands. The bulky groups, while electronically innocent, effectively influence the electronic properties of the complex through steric interactions. The 3 position on the pyrazole ring provides optimum placement for bulky groups to lengthen the ligand-to-metal bond. The electron withdrawing properties, in combination with its ability to form coordination bonds to transition metals, makes the cyano group quite valuable. Cyanoscorpionates, therefore, have the potential to form multinuclear transition metal complexes and coordination polymers. Both bulk magnetism and electrical conductivity may be achieved by the formation of a fully conjugated pathway in cyanoscorpionate coordination polymers.³

To obtain the $\text{Bp}^{\text{Ph},4\text{CN}}$ ligand for $\text{Bp}^{\text{Ph},4\text{CN}}\text{Tl}$ crystal growth, $\text{Hpz}^{\text{Ph}4\text{CN}}$ and $\text{Bp}^{\text{Ph},4\text{CN}}\text{K}$ were synthesized as described in the literature.^{12,3} The growth of x-ray quality crystals was attempted for the $\text{Bp}^{\text{Ph},4\text{CN}}\text{Tl}$ complex but further research is needed to confirm the quality of the crystals produced.

$\text{Hpz}^{\text{t-Bu},4\text{CN}}$ was used as starting material for the $\text{Bp}^{\text{t-Bu},4\text{CN}}$ ligand and was also synthesized as described in the literature.¹² The $\text{Bp}^{\text{t-Bu},4\text{CN}}$ ligand was produced for the first time by using the same synthetic procedure as the $\text{Bp}^{\text{Ph},4\text{CN}}$ ligand. Only a slight modification in the reaction temperature was needed to obtain the $\text{Bp}^{\text{t-Bu},4\text{CN}}\text{K}$ complex. Synthetic procedures were written for the synthesis of the $\text{Bp}^{\text{t-Bu},4\text{CN}}\text{Tl}$ complex and for the production of the x-ray quality crystals that lead to its structural characterization.

From the preliminary crystallographic data we have obtained, it is clear that the electron withdrawing properties of the cyano group is transferred through the ring, lengthening the thallium ligand bond when compared to $\text{Bp}^{\text{t-Bu}_2}\text{Tl}$. Further analysis shows that cyano nitrogen atoms are in close contact with neighboring thallium ions. This arrangement of molecules makes the possibility of forming a coordination polymer look promising. In addition to a lengthening of the metal ligand bond in comparison to $\text{Bp}^{\text{t-Bu}_2}\text{Tl}$, there was also a lengthening when compared to the $\text{Tp}^{\text{t-Bu}, 4\text{CN}}\text{Tl}$. While this effect was not as predicted, it is understandable when pocket stabilizing effects are taken into consideration.

Further investigation of the properties of this ligand were pursued in our attempts to form transition metal complexes. Making the $(\text{Bp}^{\text{t-Bu}, 4\text{CN}})_2\text{Cu}$ complex could result in a precursor for making two dimensional coordination polymers that would display bulk magnetism. Of the two methods used to make $(\text{Bp}^{\text{t-Bu}, 4\text{CN}})_2\text{Cu}$, starting with copper(II) nitrate appears to be more successful. At this point only IR data have been attained, so we cannot be certain of the exact molecular arrangement.

Due to the obvious advantages, molecular materials may in time out perform many traditional atom based material. Polypyrazolylborates continue to prove themselves to be a suitable ligand for use in a wide variety of applications. While the effects of the cyano substituent have not be explored to their full extent, cyanoscorpionates appear to be very promising for use as precursors for molecular magnets and conductive polymers.

BIBLIOGRAPHY

1. N. Zhao, J. C. Bullinger, M. J. Van Stipdonk, C. L. Stern, D. M. Eichhorn; "Cyanoscorpionates: Synthesis and Crystallographic Characterization of One-Dimensional Cu(I) Coordination Polymers" *Inorg. Chem.* **2008**, *47*, 5945.
2. J. S. Miller, A. J. Epstein; "Organic and Organometallic Molecular Magnetic Materials - Designer Magnets" *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385.
3. Christopher J. Siemer, Niranjana Goswami, Pawan K. Kahol, Michael J. Van Stipdonk, David M. Eichhorn; "Dihydrobis(4-cyano-3-phenylpyrazol-1-yl)borate: Homoleptic Mononuclear Cobalt(II) and Copper(II) Complexes with a Cyano-Substituted Scorpionate Ligand" *Inorg. Chem.* **2001**, *40*, 4081.
4. H.O. Stumpf, Y. Pei, O. Kahn, J. Sletten, J.P. Renard; "Dimensionality of Mn(II)Cu(II) Bimetallic Compounds and Design of Molecular Magnets" *J. Am. Chem. Soc.* **1993**, *115*, 6738.
5. A. Pron, P. Rannou; "Processible conjugated polymers: from organic semiconductors to organic metals and superconductor" *Prog. Polym. Sci.* **2002**, *27*, 135.
6. Christopher J. Siemer, F. Alex Meece, William H. Armstrong, David M. Eichhorn; "Iron, Copper, and Cobalt Complexes of Hydrotris(3-phenylpyrazolyl)borate and Dihydrobis(3-phenylpyrazolyl)borate. Synthesis and X-ray Crystallographic Characterization" *Polyhedron* **2001**, *20*, 2637.
7. N. Zhao. Cyano-substituted polypyrazolylborate metal complexes. Ph.D. Dissertation, Wichita State University, Wichita, KS, 2005.
8. (a) H.V.R. Dias, H. Lu, R.E. Ratcliff, G. Simon; "Synthesis and Structure of [Hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borato]potassium" *Inorg. Chem.* **1995**, *34*, 8, 1975; (b) H.V.R. Dias, H. Lu; "Copper(I) Carbonyl Complex of a Trifluoromethylated Tris(pyrazolyl)borate Ligand" *Inorg. Chem.* **1995**, *34*, 21, 5380.
9. Arnold L. Rheingold, Christopher D. Incarvito, and Swiatoslaw Trofimenko; "Dihydrobis(4-cyanopyrazol-1-yl)borate, [Bp4CN], a Functionalized Heteroscorpionate Ligand with Cross-Linking Potential" *Inorg. Chem.* **2000**, *39*, 5569.
10. C. J. Siemer, M. J. VanStipdonk, P. K. Kahol, D. M. Eichhorn; "A coordination polymer from a cyanoscorpionate complex" *Polyhedron* **2004**, *23*, 235.
11. J. C. Bullinger, D. M. Eichhorn; "Cyanoscorpionates: Co(II), Mn(II), and Ni(II) complexes coordinated only through the cyano group" *Inorg. Chem. Acta* **2009**, *362*, 4510.

12. N. Zhao, M. J. Van Stipdonk, D. M. Eichhorn; "Synthesis and crystal structures of 3-*tert*-butyl-4cyano pyrazole and its complexes with cobalt(II), manganese(II), and copper(II)" *Polyhedron* **2007**, *26*, 2449.
13. Ninfeng Zhao; unpublished results.
14. C. Dowling, P. Ghosh, G. Perkin; "Structural Characterization of bis(pyrazolyl)hydroborato thallium complexes: monomeric "two coordinated" thallium derivatives supplemented by [Tl...H-B] interactions" *Polyhedron* **1997**, *16*, 3469.
15. P. Ghosh, A. L. Reingold, G. Parkin; "Synthesis and Molecular Structure of Bis(pyrazolyl)hydroborato Thallium{[Bp]}₂: A [BpRR']Tl Complex with an Unbridged Close TlI...TlI Contact" *Inorg. Chem.* **1999**, *38*, 5464.
16. G. E. Buono-core, A. H. Klahn, F. Aros, V. Astorga; "Communication Benzophenone Sensitized Photochemistry of a Copper(II) Polypyrazolylborate Complex" *Polyhedron* **1996**, *15*, 363.

VITA

DONALD M. JOHNSON JR.

Personal Data: Date of Birth: April 18, 1985
 Place of Birth: Bristol, Tennessee
 Marital Status: Single

Education: Tri-Cities Christian School,
 Blountville, Tennessee 2003
 A.S. Northeast State Technical
 Community College, Blountville,
 Tennessee 2005
 B.S. King College, Bristol Tennessee
 2008
 M.S. East Tennessee State University,
 Johnson City, Tennessee 2010

Professional Experience: Volunteer, Christian Medical and
 Dental Association, March 2004-
 April 2004
 Intern, Answers in Genesis Museum,
 June 2006-July 2006
 Lab Analyst/Intern, Eastman Chemical
 May 2007-Aug 2007
 Teaching Assistant, East Tennessee
 State University, 2009-2010
 Technician, Don Johnson's Door
 Service, 2000-Present

Honors and Awards: Phi-Theta-Kappa